TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

ROOSA SILASTE

SEDIMENT QUALITY MONITORING PLAN FOR QUINTERO BAY

Master of Science Thesis

Examiner: professor Jukka Rintala
Examiner and topic approved by the Faculty council of faculty of Natural Sciences on 26th of 11 2017

ABSTRACT

ROOSA SILASTE: SEDIMENT QUALITY MONITORING PLAN FOR QUINTERO BAY
Tampere University of Technology
Master of Science Thesis, 53 pages,
November 2017
Master's Degree Programme in environmental and energy engineering
Major: Water and waste management
Examiner: Jukka Rintala

Keywords: heavy metal, sediment, sediment quality guidelines, sediment toxicity, Quintero Bay

Marine sediment contamination by persistent pollutants such as heavy metals poses one of the worst problems to marine ecosystems. Currently in Chile, there are no mandatory environmental quality standards for coastal sediments. This is partly due to lack of environmental legislation as well as insufficient toxicity data and appropriate sediment monitoring techniques.

The Quintero bay, located in Valparaiso province in the coastal area of Central Chile, was used for this study. The industrial complex of Quintero Bay is considered one of the largest in Chile and has approximately 14 companies in current operation, including cement plants, copper smelters, copper concentrators and four coal fueled thermoelectric plants. The aim of this research was to examine the current status of heavy metal pollution of the sediments in Quintero Bay in order to forward the development of any future sediment environmental quality standards (EQS) or monitoring programs in Chile. The study focuses on the heavy metal concentrations in the marine sediments. Several studies of contaminated sediments in Quintero Bay have been carried out and the results obtained from four different sources have been analyzed in this study.

Heavy metal concentrations were determined and compared to existing sediment quality guidelines. Almost all of the results of the previous studies indicate that all metal concentrations, except arsenic and copper, fell within the lower end of the sediment quality guideline range. This may signify that those metals from the sediments pose little to no potential threat to the marine organisms. Based on the Canadian SQGs, arsenic and copper will most likely cause adverse biological effects. The Quintero Bay could be categorized as unpolluted to slightly polluted marine environment, so it is important to monitor and evaluate the possible impacts of heavy metals in the sediments. Since the legislation is not available in Chile, it is advisable to evaluate the results with some of the existing EQS, and use the data for establishing local sediment quality guidelines in the future.

PREFACE

I would like to thank my examiners. They provided valuable feedback and guided me through the writing process. I am grateful for their guidance and support. Also, without the financial aid of TUT grant and MVTT this work would not be possible.

Secondly, I would like thank my employer, Ministero del Medioambiente Valparaiso [Ministry of Environment] for giving me the possibility to work on my thesis during my practice. They always encouraged me to conclude my studies and also gave me ideas for the thesis.

I would also like to thank my family and friends. They have always been supportive of me no matter what I do.

Helsinki, 26.11.2017

Roosa Silaste

CONTENTS

LIST OF FIGURES

ABBREVIATIONS

CCME	The Canadian Council of Ministers of the Environment
CEA	El Centro de Estudios Ambientales The center of environmental studies
CODELCO	National Copper Corporation of Chile
EQS	Environmental Quality Standard
EPA	The Environmental protection agency
ERA	Environmental risk assessment
EU	European Union
IFOP	Instituto de Fomento Pesquero The Fisheries Developement Institute
POAL	El Programa de Observacion del Ambiente Litoral The Costal Environment Observation Program
ROM	Recomendaciones de Obras Maritimas Maritime Works Recommendations
SEREMI	Secretarìas Regionales Ministeriales
SQS	Sediment quality guideline
WDF	Water Framework Directive

1. INTRODUCTION

Anthropogenic sediment contamination by persistent pollutants, such as heavy metals, constitutes one of the biggest impacts to marine ecosystems. Fast industrial development has resulted in increasing contamination by heavy metals that pose a significant environmental risk for living organisms (Uluturhan and Kucuksezgin, 2007). Chemicals and heavy metals may enter aquatic ecosystems through natural processes or anthropogenic activities. The major anthropogenic sources of contaminants are industrial sources such as coal, oil, fertilizers, chemicals, pesticides, mining and smelting, urban wastes, wastewater discharges and agriculture (El-Sorogy et al., 2012).

Over the past 20 years, maritime traffic has increased and although environmental regulations are stricter, contaminants are discharged into the sea, in many cases illegally (EMSA, 2012). Pollutants end up to the aquatic environment mainly directly from land-based sources, but there are occasions where they are emitted in the marine environment itself, through shipping, mariculture, offshore activities, seabed mining and sediment dredging etc. (Tornero & Hanke, 2016).

Contaminated sediments may cause a severe threat due to their ability to accumulate toxic and hazardous substances, including heavy metals, to levels many times higher than in the water column (Morillo et al., 2008). The worst property of such metals is that they are highly bioavailable but not biodegradable. In marine ecosystems, the contaminants may accumulate over time and sediments might act as a sink for heavy metals (Ridgeway et al., 2002).

The sediments work as long-term reservoirs of pollutants and can significantly affect organisms living in aquatic environments, both directly and indirectly. Bottom sediments represent an important part of coastal environment providing habitat for a large scale of benthic organisms as well as providing a substrate for aquatic plants. Therefore, the presence of harmful substances in sediments poses a significant risk to the health of the aquatic flora and fauna, because contaminants may be directly or indirectly toxic to them. Due to the ecological importance of sediments, the marine sediment quality management forms an important part of the environmental assessment (Silva et al., 2004).

Sediment quality assessment for the effects of toxic substances frequently use a triad that consists of measures of chemical concentration, benthic infaunal community structure, and sediment toxicity (Long & Chapman, 1985). Sediment is a complex matrix and therefore it is important to use a combination of different methods. Sediment quality guidelines are scientific tools that provide information of relationships between the concentration of

certain contaminants in the sediment and any harmful biological effects resulting from exposure of these pollutants. Contamination of aquatic environments may be reduced through stricter emission permits, and setting environmental quality standards (EQS) may help to prevent that the sediments or water column will not be “overloaded” with harmful substances (Brils, 2008).

The aim of this study was to examine the status of metal pollution of the sediments in Quintero Bay, Chile, due to the ecological importance of sediments in aquatic environments, and to help the progress of any future environmental legislation and sediment monitoring program in Chile. Several studies of contaminated sediments in Quintero Bay have been carried out, but there is a little analysis or comparison with other sources. Therefore, heavy metal concentrations found in the bay were interpreted using existing sediment environmental quality standards (EQS), and compared with other regions of the world in order to examine the current status of the heavy metal pollution in Quintero Bay.

2. BACKGROUND

Heavy metal contamination in the marine sediments poses one of the biggest impact to littoral ecosystems around the globe. Sediment quality guidelines (SQS's) are scientific benchmarks that provide information of relationships between the concentration of certain pollutants in the sediment and any harmful biological effects resulting from exposure of these compounds.

2.1 Contaminated sediments

Sediment is known as the particulate material that lies at the bottom of aquatic environments, consisting of terrestrial material (eroded soil or rock), organic matter and minerals (US EPA, 2005). Sediments represent essential elements of aquatic environments, because many aquatic species live in the sediment and they provide a stable substrate for many organisms. The top 10 cm layer of the sediment forms the biologically active layer. This top layer acts as a habitat for micro-organisms and higher trophic level sediment dwelling and sediment-feeding organisms, such as benthic invertebrates and fish, as well as providing a substrate for aquatic plants (Burkhard et al., 2005). In addition, the microbial processes in the sediments produce regeneration of nutrients and it is an important part of the nutrient cycles for the aquatic ecosystem. Therefore, due to the important role they play, sediments represent essential elements of aquatic ecosystems.

Contaminated sediments cause a severe threat to the aquatic environment due to their ability to accumulate many kinds of toxic and hazardous substances to higher levels than in the water column. Marine sediments can also act as permanent and latent sources of re-entry of metals into the aquatic system, due to different sediment transport mechanisms (Botté et al., 2010). Natural mechanisms of sediment transport are for example, changes in environmental conditions (eg. tidal currents, waves, wind), activities of benthic organisms and mineralization processes at the water-sediment interface (adsorption, absorption, formation of sulfides). Artificial transport mechanisms are for example dredging, reworking, and changes in temperature, pH and oxygen (Duarte et al., 2010).

Sediments are generally considered to be polluted if they contains toxic or hazardous material on levels that may affect the environment or the human health (US EPA, 1998). Once contaminated, they represent an important concern for the environment for many reasons. First, aquatic sediments act as sinks for a wide variety of different persistent pollutants. Many of them have been demonstrated to be harmful to aquatic organisms such as fish and sediment-dwelling organisms (Ingersoll et al., 1997). Exposure to polluted sediments may cause many harmful impacts such as decreased survival growth

and/or impaired reproduction in benthic organisms and fish. In addition, some contaminants in the sediments are taken up through bioaccumulation (Ingersoll et al., 1997).

The term bioaccumulation refers to the uptake and accumulation of organic and/or inorganic pollutants by organisms from their environment. In other words, it is a process where the contaminants are passed along to other organism through two uptake roads; from aqueous uptake of water-borne chemicals or dietary uptake by ingestion of contaminated particles. Bioaccumulation of heavy metal depends on the bioavailability of each metal in the environmental (Chapman et al., 1996). It is a complex process resulting from interactions between various uptake routes, excretion, passive release, and metabolism (Streit, 1998). Therefore, contamination in marine sediments might pose a potential threat to bigger organisms in the top of the food chain, including humans, through consumption of seafood that contains bioaccumulated pollutants (UNEP, 2013).

Anthropogenic processes affect biogeochemical cycles in two ways: through changes in the speed at which metals are transported between different reservoirs, and by altering the original form in which they are deposited (Benjamin & Honeyman, 1992). Regardless of this, sediments usually behave as sinks for potentially polluting elements for a long time. For this reason, heavy metal concentrations in sediments are usually higher than the concentrations found in the water column. In fact, the analysis of the heavy metal content in water has some disadvantages, such as low concentrations in water, and great spatial and temporal variability (Paredes, 1998). For this reason, sediments are widely used as indicators of pollution in marine ecosystems (Soto, 2001).

Traditionally, concerns in aquatic environments have primarily focused on water quality and initiatives undertaken in the last decades have undeniably improved the condition of water quality. More recently, it has been discovered that management efforts directed only to water quality may not provide the only basis for protecting aquatic ecosystems (Spellman, 2016). Therefore, sediments play an important role in the water resource management.

2.2 General behavior of heavy metals in marine ecosystems

Heavy metals are usually defined as elements with high density (more than 5 g/cm^3) and are often found naturally forming part of the Earth's crust in different concentrations (Fergusson, 1990). Some metalloids that may lead to toxicity at low level of exposure, such as arsenic, are also considered as heavy metals with the assumption that heaviness and toxicity are inter-related (Duffus, 2002). Heavy metals are part of the natural biogeochemical cycles and move on the earth through the hydrological cycle (Salomons & Förstner, 1984), passing through all compartments of the ecosystem but with different residence times, which may vary to hundreds, thousands or millions of years, transforming into temporary or semi-permanent reservoirs until re-mobilized (Ip et al., 2007).

Normally, metals related to living organisms may be separated in 3 classes: essentials, nonessentials and borderline. These three classes of metals and metalloids relatively to living organisms are presented in the table 1 (Chiarelli et al., 2014).

Table 1. *Types of metals and metalloids relatively to living organisms. (Chiarelli et al., 2014)*

Types of heavy metal	**Heavy metals and metalloids**
Essential	Calcium (Ca), Magnesium (Mg), Manganese (Mn), Potassium (K), Sodium (Na), Strontium (Sr), Zinc (Zn), Iron (Fe), Copper (Cu)
Non-essential	Cadmium (Cd), Mercury (Hg), Silver (Ag) Tallium (Ti), Lead (Pb)
Borderline	Chromium (Cr), Cobalt (Co) Nickel (Ni), Arsenic (As), Vanadium (V), Tin (Sn)

The essential heavy metals work in various physiological and biochemical functions in living organisms. They play important roles in numerous oxidation-reduction reactions and work as a constituent of several key enzymes (WHO, 1998). Other metals, such as arsenic (As), cadmium (Cd), lead (Pb), and mercury (Hg) have no essential biological functions and are considered as non-essential metals.

Heavy metals enter to aquatic ecosystems through natural processes or anthropogenic activities. The major anthropogenic sources of contaminants are industrial sources such as coal burning in power plants, oil, fertilizers, chemicals, pesticides, mining and smelting, urban wastes, wastewater discharges and agriculture (Bryan & Langston 1992, El-Sorogy et al., 2012). Anthropogenic pollutants reach the aquatic environment mainly directly from land-based sources, but also through several activities in the ocean itself including shipping, mariculture, offshore activities, seabed mining and sediment dredging (Tornero & Hanke, 2016). Heavy metals can also be carried into waterbodies from diffuse sources with the runoff or erosion of soil, through chemical spills and through air emissions (US EPA, 2005). Natural phenomena, such as volcanic activity and weathering, also contribute to heavy metal pollution (Fergusson, 1990).

Different metals from both anthropogenic and natural sources can accumulate in sediments and soils and these substances are transported to water and sediments both directly and indirectly through a variety of pathways. It's been generally shown that heavy metal uptake through the food chain occurs mostly from food, water, and the sediments. However, effectiveness of heavy metal uptake from different sources may differ, depending on metabolism of each organisms, in which form the contaminant is present as well as

other factors such as temperature, salinity and interacting agents (Heath, 1987, Langston, 1990).

Persistent and non-biodegradable heavy metals cause serious eco-toxicological impacts. The worst property of thos metals is that they are highly bioavailable but not biodegradable (Morillo et al., 2008). Adverse effects of heavy metals to marine organisms are for instance changes in their morphology, physiology (growth, development, swimming ability, breathing and circulation), changes in biochemistry (blood chemistry, enzymatic activities), and changes in behavior and reproduction (Bryan, 1976), causing gradual degradation of the affected ecosystem, producing mortality mainly in the larval and juvenile stages (Soto, 2001). In marine ecosystems, energy flows from the base (detritus, phytoplankton, macroalgae, halophyte plants) to higher predators (invertebrates, fish, birds) (Soto-Jiménez, 2011). Heavy metal bioaccumulation in aquatic organisms depends on many factors such as age, size, habitat preferences, eating habits, trophic level, duration of heavy metal exposure and homeostatic regulation activity (Sankar et al., 2006). For instance, filtering species and planktonic organisms are more exposed to heavy metals dissolved in water (Salomons & Förstner, 1984).

Certain species can regulate the essential metal concentrations in their tissues. For example, mussels can regulate internal levels of trace metals more effectively than oysters, even though they have very similar feeding preferences (Reidel et al., 1995). Mollusks for instance are known to be efficient accumulators of heavy metals and have been utilized to obtain information of the quality of aquatic environments, and to quantify the effects and exposure of pollutants in their ecosystem (Markert et al., 1999). Heavy metals are accumulated because of limited ability of mollusks to excrete pollutants directly after their uptake, and lack of efficient inactivation mechanisms, such as inactivating heavy metals by binding them to metallothioneins. Therefore, the concentrations of metal in their body reflect quantitatively the levels of pollution of the environment and mollusks can be used as a key species in environmental studies (Oehlmann & Schulte-Oehlmann, 2003).

2.3 Particular behavior of arsenic, cadmium, lead, mercury and copper in the environment

A toxic heavy metal refers to any metal with high density or metalloid that is noted for its potential toxicity (Srivastava & Goyal, 2010), especially in environmental contexts. The term "toxic" has particular application to arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg). Those metals are considered to the most toxic metals to the environment, including humans, according to report of the Agency for Toxic Substances and Disease Registry (ATSDR), where arsenic, lead and mercury are at the first, second and third position in the priority list called 'Top 20 Hazardous Substances'. Cadmium holds the 7th place (Govind & Madhuri, 2014).

Unlike these four non-essential metals, copper (Cu) is an essential trace metal, which is required in low concentrations for living organisms as it works as a cofactor for more than 30 different metabolic enzymes and maintains the cellular functions (Monteiro et al., 2009). Cuproenzymes use copper's ability to cycle between an oxidized and reduced state, Cu(II) ->Cu(I), that is involved in redox reactions. However, these transitions between Cu(II) and Cu(I) can result in the generation of hydroxyl radicals, which makes copper potentially toxic (Stern, 2010). For example, free cupric ions in higher concentration have been indicated to be toxic for marine organisms (Nor, 1987).

Heavy metal carcinogenicity and toxicity involves many aspects that are not fully understood. However, each metal is known to have unique properties and features related to its specific toxicological mechanisms. The effects of exposure associated with these five metals (As, Cd, Pb, Hg and Cu) are shown in table 2.

Table 2. *Main effects associated with As, Cd, Pb, Hg and Cu (Govind & Madhuri, 2014)*

Metal	**Effects on living organisms**
Arsenic	Arsenic probably carcinogenic and toxic trough exposure by drinking water (Ferguson & Gavis, 1972). Organic arsenic is highly toxic and it can cause gastrointestinal problems, severe impacts in the cardiovascular trough ingestion, central nervous system and eventually death (Haileslassie & Gebremedhin, 2015). Arsenic's bioavailability and toxicity depend on its chemical form or species in the marine environment (Cullen & Reimer, 1989). Water-soluble inorganic As is easily absorbed from digestive system. High concentrations of inorganic As can cause infertility, skin disturbances, heart disruptions, brain damage and death. The LD_{50} (oral) of As varies from 10-300 mg/kg.
Cadmium	Cadmium is a highly dangerous environmental pollutant causing different types of damage (Ciliberti et al., 2011). Cd is highly toxic, it is eliminated slowly and it penetrates easily the cells through different transport mechanisms. Cd accumulates in organs throughout lifetime and has a long (17-30 years) biological half-life (Goyer, 1997). It can cause damage to immune system and kidneys, bone fractures, reproductive problems, stomachaches, vomiting and diarrhea. The LD_{50} (oral) of Cd ranges from 63-1125 mg/kg in animals (Govind & Madhuri, 2014).
Lead	Lead concentrations more than 30.2 mg/kg may cause hazard to sediment-dwelling organisms (CCME, 1995). It has adverse effects to survival, growth and metabolism of living organisms. Lead may enter to the body through inhalation and ingestion. Its maximum allowable level in bottled water is 5µ g/L. It may cause disruption of hemoglobin's biosynthesis, anemia, kidney damage, reproductive/fertility problems and neurotoxicity (Franson & Pain, 2011).
Mercury	The organic form of mercury is more toxic than inorganic Hg because it's more easily absorbed into living organisms. The toxicity effects of mercury are disruption of nervous system, kidney damage, damage to brain and DNA, and birth defects and miscarriages. Mercury's LD_{50} is only 1 mg/kg in small animals (Govind & Madhuri, 2014)
Copper	Copper concentrations more than 20 micrograms per gram (µg/g) have been shown to be toxic for the marine organism (Wright & Welbourn, 2002) and causing physiological changes such as a stall in the growth in studied organisms (USEPA, 2007). LD_{50} values depend on animal species and route of exposure. Values between 32 and 1600 mg/kg have been reported after a single oral exposure (WHO, 1996)

Due to their possible toxicity, the use of certain heavy metals is nowadays restricted or banned. Since the late 1970's, lead exposure has decreased, resulting from many efforts to eliminate lead in petrol, and lead level reduction in cans, paints and plumbing systems

(ATSDR, 1999). Mercury's industrial demand peaked in 1964 and began to steeply decline 1980's, resulting from bans on mercury additives in pesticides, paints, and the reduction of use of mercury in batteries (USEPA, 1997). Although cadmium is still use in batteries, its commercial use has declined in developed countries (USEPA, 2006), in response to environmental concerns.

However, not all metal use has been restricted. For many years, organotin tributyltin (TBT) was used as an active component in antifouling paints, which have been found to have an endocrine disrupting effect on shellfish (Dafforn et al., 2011). Since 2008, TBT-paints were globally prohibited and biocides such as copper salts (for example copper oxide (Cu_2O)), have been used as main TBT alternatives in antifouling coatings. Therefore, maritime transport is considered as an increasing and significant anthropogenic copper source to the marine environment (OSPAR, 2010). Although copper is assumed to be less toxic than TBT, it may have negative impact to aquatic organisms in higher concentrations than physiologically necessary (Karlsson et al., 2010)

The source, chemical form, and accumulation habit associated with these five metals (As, Cd, Pb, Hg and Cu) are shown in table 3.

Table 3. *Source, chemical form and metal accumulation of As, Cd, Pb, Hg and Cu*

Metal	**Source**	**Chemical form**	**Accumulation**
Ar	The largest sources of anthropogenic arsenic pollution are chemicals used in agriculture, such as fungicides, herbicides, rodenticides and insecticides (El-Sorogy et al,. 2015) as well as fossil fuels and mining (Bissen & Frimmel, 2003).	Arsenic has many organic and inorganic forms. The most common form of inorganic arsenic is arsenate (As^{5+}; AsO_4^{3-}). Other possible forms of arsenic are arsenate (As^{3+}; AsO_3) and organic forms such as dimethylarsinic acid, monomethylarsonic acid and arsenobetaine (Shiomi, 1994).	Fine particle sediments tend to absorb arsenic. Although arsenic is found in aquatic organisms, it does not progressively concentrate along a food chain. Therefore consumption of arsenic containing aquatic organisms does not pose potential hazard to humans, unlike ingestion of drinking water with high concentrations of arsenic (Ferguson & Gavis, 1972).
Cd	Mining, agriculture and discharges of industrial and municipal wastewaters are the main sources of anthropogenic cadmium (Järup & Åkesson, 2009). Cd is also used in many industrial activities: alloys, pigments, and batteries.	Cadmium usually has an oxidation state of +2, but it also exists in the +1 state (Holleman, 1985).	It is highly bio-accumulative and extremely toxic (Ciliberti et al., 2011). Cd has low solubility in water phase, but it is easily adsorbed on organic matter and therefore it accumulates in the sediment. As a matter of fact, the Cd concentration in the sediment reflect the degree of contamination for the water phase (Selvaraj et al., 2004).

Pb	Lead compounds originate from petrol, due to its historical use in combustibles. It is also present near lead mines and smelters, urban and industrialized areas, areas of recycled lead batteries and sewage and disposal areas (Wright and Welbourn, 2002).	Lead compounds are usually found in the +2 oxidation state rather than the +4 state, which also exist (Wright and Welbourn, 2002).	Lead accumulates in the sediments, but it does not bioaccumulate up in the food chain. However, lead has been shown to bioaccumulate in fish's skin, bones, kidneys, and liver, and therefore people and animals that eat fish may be exposed to high lead concentrations (Wright and Welbourn, 2002).
Hg	Mercury is utilized widely in numerous industrial processes, for instance the production of caustic soda, in the electrical industry, pharmaceutical production and as an antifungal agents in wood processing (Tchounwou et al., 2003).	Mercury is a silvery-white metal, with low melting point, and it exist in three different forms: organic, inorganic and elemental (Graeme et al., 1998). Inorganic mercury might be converted into methylmercury, due to the bacterial activity in the sediments. Lipid soluble methylmercury is 10 to 100 times more biologically available than inorganic Hg.	Hg accumulates easily in food chain and in the sediment, where it can be easily transferred. Most of mercury compounds bounds to particles, colloids and other organic matter with high molecular weight (Schiff, 2000). Lipid soluble methylmercury is easily dissolved to the water phase from the sediments and therefore becoming more bioavailable. It bioaccumulates up in the marine food chain, leading to increased concentrations especially organisms in top of the food chain. (Schiff ,2000).
Cu	Copper discharges comes from anthropogenic sources, such as mining, production and refining of copper, industrial/domestic waste water, antifouling coatings, wood production, combustion processes and production of phosphate fertilizers. (Dafforn et al, 2011).	Copper exists in natural water systems either as a cupric (Cu^{2+}) ion (dissolved form) or absorbed to organic matter or suspended particles or as complexed with inorganic anions or ligands such as carbonates and chlorides. Copper may also be adsorbed to sediment or exist as settled precipitates (Mance et al., 1984).	The small quantities of Cu required to maintain physiological and morphological normality of growth in aquatic organisms. However, excessive accumulation of copper in organisms is potential hazard to biological processes. Field and laboratory studies on have shown that essential metals like Cu are more highly accumulated than nonessential metals (Anan et al., 2005).

2.4 Sediment remediation

There are several remediation strategies that have been used successfully with contaminated sediments. Usually, sediment remediation utilizes physical, chemical and/or biological treatment technologies in order to reduce pollutant concentrations or mobility in the sediment. Remediation techniques function by separating, breaking down or converting the contaminants from the sediment into less toxic forms or by stabilizing the contaminants to solids and in this way reducing the transport of pollutants to aquatic environments (ICSUNIDO, 2007; Ingersoll, 1995). Of all the sediment remediation technologies available, removal-based technologies have been in existence the longest, and are thus the most well-known. New removal approaches are for example sediment resuspension methods that are based on removal of finer sediments (Pourabadehei & Mulligan, 2016).

Sediment remediation is a complex process, because there are many factors that have to be taken into consideration. Understanding and predicting the behavior of contaminants and anthropogenic events in a dynamic environment is often challenging (US EPA, 2005). The contamination to which sediment is exposed may be difficult to control, it may be diffused and the remedial actions usually cause some disturbance and possible release of contaminants into the environment (ICSUNIDO, 2007). The site may not be acutely toxic to the aquatic ecosystem (e.g. due to risks arising through bioaccumulation), even though it is considered contaminated. Thus the sediment may contain ecologically valuable resources, and even endangered species or habitats. Furthermore, the aquatic environment poses technical challenges for remedial action, and the remediation is often more costly than in the case of other media (US EPA, 2005).

The most commonly used remediation techniques for contaminated sediments are dredging or excavation, monitored natural recovery and active or passive capping. These globally-accepted technologies rely on either removing contaminated sediment, then managing it *ex-situ*, or remediating sediment contamination in-place (*in-situ*). Less frequently used in-situ methods generally aim to enhance degradation of the contaminants and involve techniques such as biological, chemical and thermal treatment (US EPA, 2005; ICS-UNIDO, 2007). Usually, a final sediment remedy combines more than one type of approach. Ex-situ sediment remediation could instead be accomplished using the much newer and non-conventional technique of freeze dredging (Rostmark et al., 2015).

"No action" is a good alternative in those cases, when the situation after the remediation process might be worse than the original situation—e.g., when remediation techniques, such as dredging, cause more damage than for example leaving the sediment in place. If the source of contamination is controlled, new sediment layers will cap the contaminated area over time, because contaminants generally accumulate in depositional zones (Demars et al., 1995).

2.4.1 *Ex-situ* sediment remediation techniques

The removal of contaminated sediment from the waterbody is called dredging. When the water has been diverted or drained prior to removal of the sediment, the term excavation is used (US EPA, 2005). *Ex-situ* sediment remediation typically involves the following steps: (1) physically removing contaminated sediments from the aquatic environment by dredging (surface water present) or excavation (surface water absent), (2) removing pore water from the sediment, (3) treating the separated solid and/or pore water phases, and (4) transporting and disposing of the sediment solids (Jersak et al., 2016). Of all the sediment remediation technologies available, removal-based technologies have existed the longest, and are thus the most well-known.

Various types of dredgers are used in sediment remediation and the dredgers can be divided generally into two categories, depending on the basic means of moving the sediment. With the mechanical dredgers the sediment is lifted mechanically with buckets and with the hydraulic one, the sediment is moved through a pipe (US EPA, 1994). Dredging contaminated sediments tends to release contaminants into the surrounding water or into the atmosphere, which is a particular concern of this method. The organic contaminants usually bind to the fine sediment particles, which are most easily suspended while disturbing the sediment (US EPA, 1994). In addition, the contaminated sediment that has been removed typically requires transporting the contaminated matter from one location to another for treatment and/or disposal. The required technologies and post-processing make dredging projects complex and expensive. The benefits of dredging methods lie in the removal of contaminated sediments from the aquatic environment, in that way achieving the remedial objectives quickly and allowing flexibility in the later use of the waterbody. The relative advantages and limitations of removal-based technologies discussed in US EPA (2005) are summarized in table 4.

Table 4. *Remediating contaminated sediments by removal: Relative advantages and limitations (US EPA, 2005)*

Advantages	**Limitations**
• Contaminants removed from the aquatic environment. • Can be used to remediate a wide variety of dissolved-phase contaminant types and concentrations, multiple contaminants, and non-aqueous phase liquids (NAPLs). • Can sometimes quickly reduce contaminant exposure and related risks. • Greater certainty of long-term effectiveness. • Typically few to no restrictions on site use after removal. • Offers potential for beneficial re-use of removed sediment material.	• Often more complex and costly than in-situ capping • Contaminants often not destroyed, rather they are moved from one location to another. • Nearby disposal capacity may be limited. • At least some residual sediment contamination always remains after removal. • During removal, more disruptive to humans and the environment. • After removal, more disruptive to benthic and/or aquatic habitats. • Typically more costly than other remedial technologies

2.4.2 *In-situ* sediment remediation techniques

Several *in-situ* sediment remediation technologies, like in-situ capping, Monitored Natural Recovery (MNR) and Enhanced MNR (EMNR) are globally recognized and accepted. Monitored Natural Recovery (MNR) generally does not include any treatment, but involves allowing contaminated sediments to remain in place and letting ongoing, naturally occurring recovery processes (chemical, biological, and/or physical) to naturally contain, destroy and/or reduce bioavailability and/or contaminant toxicity over time, eventually to acceptable levels. The advantages of this technique are its low implementation expenses and non-invasive nature. However, the limitations are that the method leaves the pollutants in place and that natural processes might be slow in reducing the risks compared to other remedial methods (US EPA, 2005). Compared to other remedial technologies, MRN is more of a risk-management approach than an active remediation technology. EMNR is very similar to MNR. However, EMNR additionally involves applying a fine layer of sediment or sand to the polluted sediment surface to improve or “fast-forward” chemical, biological, and/or physical processes of natural recovery.

In-situ capping refers to covering the contaminated sediment with clean material. The contaminated sediment generally remains in place and the clean material on top of the contaminated site functions by isolating and/or stabilizing the pollutants. Granular materials, e.g. clean sediment, sand or gravel are commonly used as a capping materials. More complex cap designs may contain geotextiles, multiple layers or liners. *In-situ* capping can provide clean substrate for recolonization of benthic organisms and it may reduce the exposure of biota relatively rapidly. Generally, capping also requires less infrastructure compared to *ex-situ* techniques like dredging. The limitation of this method is that it leaves the contaminants in place and thus to some extent involves a risk that the contaminant may be re-exposed. Similarly to dredging, it also includes at least temporal destruction or severe disturbance of the aquatic community at the site (US EPA, 2005).

2.5 Environmental legislation in Chile

The main framework is given by Law No.19,300/94 (general environmental law), a framework law on environmental policy, management and oversight. The law establishes different standards (e.g. for emissions) and creates plans for prevention and decontamination. Published on March 9th 1994, this Act constitutes a basic legal framework of the whole environmental regulations of the country, making sure that the necessary tools and institutions for protecting the environment in harmony and in keeping with the constitutional precept of article 19 N°8 of the Constitution of the State are regulated and developed. Title I contains five dispositions of general character. The first article establishes that *"The right to live in an environment free of pollution, protection of the environment, preservation of nature, and conservation of the environmental heritage will be regulated by the dispositions of this act, without prejudice of what other legal dispositions establish upon this matter"*

However, the environmental regulations in Chile are unconsolidated and for example, there is no single regulatory regime and no single authority covering water or sediment pollution (Urrutia & Aviles, 2017). There are no quality standards for pollutants in sediment for instance.

2.5.1 Emission standard (Executive Decree 90/2000)

Established emission standard (Executive Decree 90/2000) for the regulation of contaminants associated with the discharge of liquid waste to marine and continental surface waters determines the maximum concentrations of pollutants allowed in discharges or emissions. The purpose of this standard is to protect the environment by preventing contamination of the marine and continental surface waters of the Republic by controlling the contaminants associated with the liquid waste that is discharged to these receiving bodies. Supreme Decree No. 90/2000 aims to regulate the discharge by setting maximum daily limits for the discharge of liquid waste, including the maximum concentrations of

heavy metals like copper and mercury. The decree establishes that any source that discharges its liquid waste to surface water must characterize its liquid waste in order to evaluate if it qualifies the requirements of the emission standard. In each case the legislation determines the maximum concentrations of pollutants allowed in discharges or emissions (DS 90/2000).

Emissions must comply with certain quality standards if they are to be discharged. In accordance with the above, each company has its own monitoring program for its effluents, depending on the company size and the type of the waste water. All companies that are discharging their wastewaters must monitor the effluent values. If values of certain pollutants in the effluent reach a certain value, the company must take steps to comply with regulation (DS 90/2000).

3. LEGAL BACKGROUND AND SEDIMENT QUALITY MANAGEMENT

In this chapter, legal background in Chile, EU and Canada is presented as well as sediment quality management strategies and guidelines.

3.1 EU water framework directive

The rising concern about harmful substances is reflected by the increasing number of European Union (EU) Directives as well as national and international conventions related to those compounds (Plant et al., 2005). Different regional and national legislations have been implemented in EU in order to decrease the use of harmful substances and to reduce their release into the environment, including marine waters and sediments. Collectively this legislation aims to decrease risks to the environment as well as human health through a variety of approaches that include for example the establishment of EQSs for aquatic ecosystems.

The European Environment Agency (EEA) and the United Nations Environment Programme (UNEP) brought forth the problem of chronic exposure to probable toxic compounds (EEA/UNEP 1999). The Water Framework Directive (WFD) is a European Union Directive (2000/60/EC) whose main objective is to accomplish a good ecological status of aquatic environments including river water, seawater, groundwater and coastal waters. It aims to establish a legal framework for the water quality protection and good chemical status in EU member states together with Environmental Quality Standards Directive (2008/105/EC).

The WFD specifies environmental quality standards (EQSs) for 33 priority substances, including heavy metals such as lead and mercury. The framework states that the emissions of priority substances, which could threaten human health or ecosystems, need to be reduced progressively. The WFD defines EQSs of annual average and maximum allowable concentration in surface water for all 33 substances.

The EQS's for most of the substances in the priority substance list (33) has been established only for the concentrations in the water column. No EQS values have so far been set in sediments under the Water Framework Directive. However, there is a clear link between sediment quality and the framework objective, and several EU countries have payed attention to sediment contamination. According to the European Commission (EC, 2010), sediment and biota are the most suitable matrices for trend monitoring of many substances, because certain pollutants accumulate in the sediments and the concentrations do not change as quickly as in the water column and long-term comparisons can be made.

The priority substance Directive (EU 2008/105/EC) gives a suggestion of the substances, which should be taken into account for trend monitoring as well as the frequency of monitoring of those chemicals. Therefore, EU countries are encouraged to perform long term trend analysis of concentrations of harmful substances, because sediments represent a good matrix for monitoring purposes. For example, with hexachlorobutadiene and mercury, EQS for surface water alone is not sufficient to ensure protection against harmful effects (EU, 2010).

Moreover, EU States should have the opportunity to establish at national level EQS for sediment and apply those sediment EQS instead of the water EQS's determined in the Directive. Member States should take measures in order to estimate long-term impacts of anthropogenic inputs and to ensure that existing levels of pollution in sediment will not significantly increase (EU, 2010).

3.2 Sediment quality monitoring

When assessing the impact of the water quality on the environment, a range of indicators are used. These indicators may be the sediments and biological matter in the water column, chemical pollutants in biota, and chemical contaminants in the bottom sediments. Sediment is a recommended assessment matrix for hydrophobic compounds and chemical status for some metals in marine environment and lentic water bodies. Sediments do not usually provide a good matrix in dynamic lotic water bodies, such as rivers, because of the high variability (Ingersoll, 1995).

Sediments are suitable matrices in trend monitoring for many contaminants, because they integrate substances in time and space and changes of concentrations are smaller than in the water column, so long-term comparisons can be made. Several factors, including chemical properties (e.g. affinity and aqueous solubility) and environmental characteristics (e.g. pH, content of organic carbon, grain size of the sediment and sediment mineral composition) affect the partitioning and sorption of compounds between water and sediment (Ingersoll, 1995). For example, fine sediments tend to absorb more metals and organic matter compared to more coarse ones (Carpentier et al., 2002).

While selecting the substances to be monitored in sediment, their physico-chemical preference for the solid phase should be taken into consideration. The compound is more likely to absorb to the sediment particles when it is more hydrophobic and therefore less soluble in the water column. The octanol–water partition coefficient (Kow) is a simple measure of the hydrophobicity of an organic substance, which is a good predictor of the partitioning potential of the pollutant in the sediment's organic fraction (Koc). The basic rule is that compounds with a log Kow>5 should preferably be measured in sediments. For example, hexachlorobenzene (log Kow=5.7) should be monitored in sediments or in suspended particulate matter, because of its preference to adsorb to organic sediment particles (EU, 2010).

Most of the monitoring programs are addressed to evaluate the effects of chemical contamination, but getting this data is often complicated (Wenning et al., 2005). The biological availability of substances in sediments is not fully understood and complex. For instance, the concentrations of contaminants in sediment may be much higher than in the water, but the bulk sediment concentration may not correlate directly to the bioavailability. Furthermore, the compounds are often present in complex mixtures and their effects are hard to predict. Sediment quality assessment for the effects of toxic substances frequently use a triad that consists of measures of chemical concentration, sediment toxicity, and benthic infaunal community structure (Long & Chapman, 1985). Sediment is a complex matrix and therefore it is important to use a combination of different methods.

Nevertheless, sediment and biota monitoring can be a useful tool to determine general contaminant status. It can also provide reference values for regional and local monitoring. Sediment monitoring is a cost-effective method for initial screening of contaminated sites, identifying possible sources of contaminants, and comparing contaminant concentrations in different areas. The initial screening helps to identify problematic areas as well as areas where more effort is needed. Water measurements may be downscaled, if sediment monitoring is being used as a first level screening for certain substances in the monitoring program (EU, 2010).

3.2.1 Sediment monitoring frequency

The frequency of monitoring of priority substances in sediments differs from those in the water column (whole water or dissolved) and it is clear that the costs and resources affects the choice of the matrix to be monitored and to the monitoring frequency. For example, Water Framework Directive (EU) states that the minimum monitoring frequency of 33 priority substances is once per month from the water column, but for the sediments the monitoring frequency may be once a year unless there is more technical knowledge to justify another interval (EU, 2010).

In the Baltic Sea, the monitoring frequency varies from 1-2 samples to 24 samples, depending on country. Finnish Environment Institute (SYKE) collects long-term observations of sea, lake, river, and groundwater water quality – for instance, on water temperature, oxygen level, salinity, turbidity, nutrients and concentrations of harmful substances. Concentrations of harmful substances in the open sea are monitored on the basis of fish samples, water samples, samples of plankton and the sediment. Fish samples are collected and analyzed every year from four different monitoring sites. Sediment samples from the open water are collected and analyzed from three different monitoring sites every second year. In coastal areas sediment samples are taken from 10 monitoring areas every three years (SYKE, 2016).

3.3 Sediment Quality Guidelines

Environmental Quality Guidelines (EQSs), also referred as Sediment Quality Guidelines (SQGs), are scientific tools that provide information of relationships between the concentration of certain contaminants in the sediment and any adverse biological effects resulting from exposure of these pollutants. (Wenning et al., 2005). SQS's provide benchmarks for evaluating the harmful biological effects in aquatic environment (CCME, 1999).

The guidelines can be roughly subdivided into two categories, depending on the approaches used to develop each SQGs. Those two categories are empirical guidelines and mechanistic guidelines. Empirically derived guidelines use databases of concentrations of certain sediment pollutants and observed adverse biological effects that are based on sediment toxicity tests and benthic community information. Plenty of different algorithms are used to define specific concentrations, for example the threshold effect level (TEL) and/or the probable effect level (PEL), that are associated with particular levels of effect or no effect. Mechanistic guidelines, on the other hand, are based on the theoretical understanding of known relationships between toxicity and chemical exposure, and the factors that govern bioavailability of sediment contaminants (SETAC, 2002).

Like other environmental quality guidelines, SQGs have a wide range of potential applications. They can be used for example as a goals or targets for toxic chemical management programs and as targets or benchmarks in the remediation and assessment of polluted sites. They can also serve as benchmarks for discussions on emission reductions, in environmental impact evaluation and for sediment quality monitoring programs. Sediment quality guidelines may be used for example to classify the toxic potential of sediment samples, identify possibly harmful pollutants and to prioritize areas based on the values that are exceeded. Depending on the guideline, there are several types of SQGs limits: those that consider the risk to aquatic life, those that evaluate anthropogenic contamination through comparison to background levels of a substance (generally heavy metals), and those that consider the risk to human health. For example, in EU water framework directive, EQS means the concentration of a particular contaminant or group of contaminants in water, sediment or biota that should not be exceeded in order to protect environment and human health (EU 2000/60/EC).

North American environmental regulators and researchers were the first developing methods for sediment toxicity testing and regulatory tools for monitoring and controlling sediment contamination (Crane et al., 1996). In Europe, regulation of contaminated sediments are less identical, with individual EU member states developing Sediment Quality Guidelines (SQGs) and monitoring strategies independently (Ahlf et al., 2002).

Different roles of SQG's as a management tool is presented in the table 5. SQGs alone are in some cases sufficient for management decision-making. Numerical SQGs, as part of an environmental risk assessment, can provide benchmarks for assessing the hazards

associated with polluted sediments in conjunction with other tools such as bioaccumulation, benthic community surveys and sediment toxicity tests (Ingersoll et al., 1997). However, SQGs alone do not provide all possible monitoring needs such as effects to human health.

Table 5. *Role of sediment quality guidelines (SQS's) (GIPME, 2000)*

Reason for sediment assessment	**Role for quality guidelines**	**Specific role of guidelines**
Mapping spatial patterns	Primary	SQGs can be used to address relative patterns of contamination, including probable no effect and possible effect concentrations in sediments
Measuring temporal trends	Primary	
Determining condition of populations and communities	Secondary	As part of an environmental risk assessment and/or in a tiered assessment scheme, SQGs are useful when used in conjunction with other tools
Estimating ecological risks, including bioaccumulation	Secondary	
Estimating human health risks and evaluation of biomagnification	None	SQGS have not been developed for this purpose

* "Primary" can be used alone for decision-making and "Secondary" should be used with other assessment tools. In most cases, site-specific information should be generated to supplement the use of SQGs in sediment assessments

3.3.1 Sediment Quality guidelines in USA

The Environment Protection Agency of United States of America (EPA or USEPA) is an agency of the federal government of the United States that was established for protecting both human health and the environment by creating and enforcing regulations based on different laws passed by the congress.

EPA's aquatic life criteria is based on how much of a pollutant can be present in aquatic environment before it is likely to harm living organisms. EPA has aquatic life criteria to protect both fresh- and saltwater organisms from short- and long-term exposure. Organisms such as worms and plants often live in the sediment at the bottom of lakes, rivers and other bodies of water. Pollutants in sediment can make their way up the food chain and threaten larger animals as well as people. For this reason, the EPA has developed guidance on developing criteria for suspended and bedded sediment (USEPA, 1998).

EPA's National Coastal Condition Report presents Coastal Sediment Quality Index, which is based on two measures: sediment toxicity and sediment contaminant concentrations (USEPA, 2004b). Field crews collect comparable sediment samples that are analyzed to determine concentrations of a suite of contaminants and subjected to sediment toxicity tests. All of these studies are conducted with a high level of quality assurance/quality control procedures.

The condition of the sediments is determined by comparing the measured concentrations to two different developed values: "effects range low" (ERL) and "effects range median" (ERM) (Long et al., 1995). Those two values identify threshold concentrations that are expected to produce adverse biological or ecological effects when exceeded. In this indicator, sediment contamination is considered moderate if five or more ERLs are exceeded and high if one or more ERMs are exceeded.

Sediment toxicity also depends on their biological availability, not only on the individual concentrations of toxic metals, which depends on e.g. pH, acid particle size, volatile sulfides, organic content, and the specific form of pollutant (e.g., methyl mercury vs. mercury). For this reason, sediment toxicity should be tested in practice by bioassays that use test organisms in order to evaluate possible adverse biological effects to each organism. In USA, sediment toxicity tests are based on 10 day static tests using the benthic amphipod (*Ampelisca abdita)*. Sediments are defined to be toxic if greater than 20 percent mortality is resulted in the bioassays, or non-toxic if the bioassays resulted in 20 percent mortality or less (EPA, 2004b).

3.3.2 Canadian environmental Quality Guidelines

Canadian Water Quality Guidelines were released in 1987, by The Canadian Council of Ministers of the Environment (CCME). These guidelines included indications for the protection of aquatic life, agricultural water uses, raw water for drinking water supply, and water supply for industrial purposes. These guidelines were the first national, science-based environmental quality guidelines, which proved that Canada was a leader in the development of such guidelines (CCME, 1995).

Sediment quality guidelines provide science-based tools for evaluating the possible adverse biological effects in aquatic environments. The Canadian environmental quality guidelines are based on the toxicological information, as well as a wide range of chemical and biological data that was evaluated from multiple individual studies in order to settle an association between the concentration of each contaminant and any adverse observed biological effect. Hence, the data was used to calculate two different assessment values, that are 1) the threshold effect level (TEL) and 2) the probable effect level (PEL). The lower value (TEL) represents the concentration where the adverse biological effects are

expected to occur infrequently. The upper value (PEL) represents the level where the harmful effects are expected to occur more often. Therefore, when exposed to TEL, effects may be observed in some sensitive organisms, whereas the upper PEL value is likely to cause harmful effects in a wider range of species (CCME, 1995).

The definitions of TEL and PEL values are based on the assumption that the potential for observing adverse effects resulting from exposure to a chemical is greater, when the concentrations of a such chemical in the sediment is also bigger (Long et al. 1995). The Canadian sediment quality guideline (ISQG) equals to the definition of TEL. The PEL can be used as an additional assessment tool, which may be useful in identifying those sediments where harmful biological effects are more likely to occur. Canadian ISQGs for fresh water and marine sediments are recommended for total concentrations of chemicals, as quantified by standardized analytical protocols for each chemical (CCME, 1995).

The proper use of different sediment quality assessment tools will provide the most serviceable information, because it is widely known that a single tool should not be used to predict if adverse biological effects will occur or not (Luoma & Carter, 1993). Therefore, Canadian ISQGs should be used alongside all other relevant information, when making decisions over sediment quality.

3.3.3 Sediment Quality guidelines in EU

As explained in the chapter 3.2, under the Water Framework Directive, no EQS values have been set in sediments and the EQS's for most of the substances in the priority substance list (33) has been established only for the concentrations in the water column. However, several EU countries have payed attention to sediment contamination and the SQG's have been established in some of the EU countries.

For example in Spain, ROM, Maritime Works Recommendations (Recomendación de Obras Marítimas), is a tool for the management of the seaport water bodies quality, that has been developed in Spain. The aim of the EU water framework directive based recommendation is to serve as a base document for port water quality management system planning, achieving this through a combination of legislative, technological and methodological aspects. Since the beginning of the 1990's, Spanish ports have been working on the improvement of marine environment, as well as all other ports in the European Union. The goal of this suggestion was to contribute to transport sustainability, harmonizing their environmental policies and developing specific tools for identification and reduction of anthropogenic impacts in ports, and for the control and management of different environmental risks. This directive was entered into Spanish law (RD 60/2011) that provides the legislative reference of water and sediment chemical quality including the EQSs for priority substances and other preferential contaminants. The indicators considered for sediment quality evaluation include all the heavy metals and polycyclic aromatic hydrocarbon (PAHs) (ROM, 2013).

3.3.4 Sediment quality criteria: overview

As it can be seen in the overview of existing sediment quality criteria, there is no world-wide harmonization, or specific international regulation of sediment quality, although some efforts have been done recently. This non-harmonization leads to existence of different reference values for a same contaminant. Some examples of sediment quality guideline values for six heavy metals (Ar, Cr, Cd, Cu, Hg, and Pb) are given in table 6 to illustrate this point.

The Dutch apply a tiered system to classify the level of contamination. The two key levels, shown in the table 6, are as follows (Warmer & Dokkum, 2002): target value (TV) –and reference value (RV). Target value indicates the level below where the risks to the environment are considered to be negligible, and reference value indicates the maximum allowable level of contaminants.

Table 6. *Standards and guidelines of chemical contamination in sediments (mg/kg dry weight)*

Organization/ country	**Quality level**	**Heavy metal**					
		Ar	**Cr**	**Cd**	**Cu**	**Hg**	**Pb**
Long et al. Sediment quality Guidelines (used in USA, EPA)	ERL effects range low	8.2	81	1.2	34	0.15	46.7
	ERM effects range median	70	370	9.6	270	0.71	218
Canadian Council of Ministers of the Environment	ISQ sediment quality guideline	7.24	52.3	0.7	18.7	0.13	30.2
	PEL probable effect level	41.6	160	4.2	108	0.7	112
Dutch quality standard: saltwater sediment guidelines	TV target value	29	100	0.8	35	0.3	85
	RV reference value	55	380	7.5	90	1.3	530

As shown in the table 6, Canadian sediment quality guidelines represent the lowest concentrations of each pollutant. For this reason, those guidelines were used as reference values for this study, based on the assumption that the potential adverse biological effect resulting from exposure to a trace metal is greater, when the concentrations of a such element in the sediment is also bigger (Long et al., 1995).

4. MATERIALS AND METHODS

The Quintero bay, located in Valparaiso province in the coastal area of Central Chile, was studied for this thesis. The main characters of the bay and the industrial history of the area are presented in this chapter.

4.1 Study area

The Quintero Bay, located in the Valparaíso Region 160 km north of Santiago, in the Quintero and Puchuncaví Counties, is one of the most important industrial and energy hubs in the country. With the country's third highest population of 1.8 million in 2012 and third smallest area of 16,396.1 km2, Valparaiso is Chile's second most densely populated area after the Santiago Metropolitan Region.

Figure 1. Location of the study area, Quintero Bay, central coast of Chile

The study focuses on Quintero bay (32°46´S, 71°33´W), located in Valparaiso region, in the Pacific coast of Central Chile (fig. 1). This is a shallow embayment, about 3 miles long and 1.5 miles wide, with a maximum recorded depth of 55-60 m (fig. 2). The Quintero bay has a horseshoe form open to the north, which offers little protection against climatic events.

Figure 2. The Quintero Bay

This bay comprises two communes of the Region of Valparaiso (Puchuncaví and Quintero) within which there are localities such as Maitenes, La Greda, Las Ventanas, Quintero, Loniche, Campiche, Puchuncaví, Chocota, Caleta Horcón, Maitencillo, Melosillas, El Runge , Ritoque, Mantagua (IFOP, 2016).

4.2 Industrial activity in the Quintero Bay

The industrial complex of Quintero Bay is considered one of the largest and most important in Chile and has approximately 15 companies in current operation, including copper smelters, cement plants, copper concentrators and four thermoelectric plants fueled by coal and petroleum coke. The industrial port sector is located in the central sector of the bay, occupying approximately 300 hectares (IFOP, 2016).

Quintero Bay has a terminal for reception, storage and regasification liquefied natural gas, which provides supply of natural gas to the central zone of Chile (ENAP, 2015). One of the most significant environmental impacts is a copper smelter, with a capacity of 110,000 tons annually. The refinery produces cathode copper, and gold, silver and selenium are produced from the anode (CODELCO, 2015).

4.3 History of environmental deterioration of the area

As a result of industrial activities in the area, the marine ecosystem has suffered different negative externalities, such as the dumping of hydrocarbons, oils or alcohols, and the escape of different chemical elements, such as heavy metals that have caused an increase in certain chemical elements outside the environment (eg copper, arsenic, lead and zinc) (Parra et al., 2015). Both the presence of heavy metals and hydrocarbons at certain levels may be considered toxic to different benthic species, and in many cases have unknown effects on the biodiversity and functioning of aquatic ecosystems (Ahlf et al., 2002).

The presence of hazardous substances in marine waters, biota and sediment in Quintero Bay has been documented by various information sources, such as the annual monitoring of the major pollutants of POAL (The Costal Environment Observation Program), but a systematic analysis of the sediment quality has not been carried out.

Three oil spills have affected the bay since 2014. On September 2014, according to a report by the Chilean Maritime Authority, 38,700 oil liters spilled into the ocean caused by a ruptured connection between the tanker and the terminal. The second and the third oil spill came right after in August 2015 and in May 2016. The environmental deterioration of the area is high. It started in the mid-60´s, when a coal-fired power plant and a copper smelter were installed in the Ventanas Sector of the bay. The pollution of the seawater, soil and especially the air has been disreputable, and in 1993, the Ministry of Agriculture declared Puchuncaví and Quintero a “saturated contamination zone” by sulfur dioxide (SO_2) and particulate matter. A decontamination plan was put into place to regulate the emissions from the two biggest sources of air pollution (coal-fired power plant and copper smelter) (Salinas, 2014).

Although the environmental situation is now better than it was earlier, the effects of decades of pollution exist. As a result of the industrial activity in the area, the marine ecosystem has suffered different negative externalities, such as the oil spills and the presence of different chemical elements, like heavy metals (Parra et al., 2015).

5. RESULTS AND DISCUSSION

The presence of hazardous substances in coastal waters, biota, and sediment in Quintero Bay has been documented by various organizations since the early 90s, but there is little comparison between different studies or international quality guidelines. The results of four recent studies made in the Quintero bay are presented in this chapter, including the annual monitoring of the major pollutants of the costal environment observation program (POAL), the ecosystem study made by the Ministry of Environment, the Fisheries Development Institute (IFOP) report, and environmental study made by Parra et al (2015).

The results of the analysis of the historical information are presented below. The first one corresponds to the lmonitoring of the coastal environment observation program (POAL). The POAL was developed to monitor annual fluctuations of contaminants, such as heavy metals and hydrocarbons, which are related to industrial activities in the coast, lakes and rivers. This program determines and evaluates the levels and concentrations of the main pollutants of both coastal and fresh waters. The second information source includes the study carried out by the center for environmental studies (CEA) under the responsibility of the Ministry of the Environment during 2012 and 2013. The third information source relates to the report of the Fisheries Development Institute (IFOP). IFOP developed a research project related to the impacts of the hydrocarbon spill in the affected area after the October's 2014 oil spill. The fourth source is the study of Parra et al. (2015), published in the Marine Pollution Bulletin, which aim was to assess the trace metal levels in the marine sediments.

5.1 Annual sediment analysis of the Environmental Monitoring Program POAL

One of the earliest monitoring program in Quintero Bay, POAL (Programa de Observación del Ambiente Litoral, the Environmental Monitoring Program), has collected information annually since 1993 from the water column, sediments and biota (ie analysis of concentrations of the species (*P. purpuratus*)). The POAL was developed to monitor annual fluctuations of the major pollutants both costal and fresh waters related to the industry in the region. The main fault found in this database is related to the lack of certainty of the analytical techniques used in the POAL before 2013, since the analytical methods are not explained and the analysis was run by a different company. For that reason, only information gained from 2013 is used for this study. However, the analyses have been carried out by the same company since 2013, so it is expected that the techniques have not changed substantially. POAL uses 14 different sediment sampling points along the Quintero Bay. From each sampling point, two samples were analyzed (POAL, 2017).

The concentrations of arsenic, mercury and copper from the last four years are presented in the figure 3. The annual mean, minimum and maximum from all the sampling points is presented in order to get a rough idea of the average heavy metal concentrations in the sediments. There was no significant correlation between different sampling points (e.g. one sampling point has higher concentration every year). The concentrations of other heavy metals, such as cadmium, did not exceed neither the detection limit nor sediment quality guideline values. For that reason, they do not pose a significant hazard to the aquatic ecosystem.

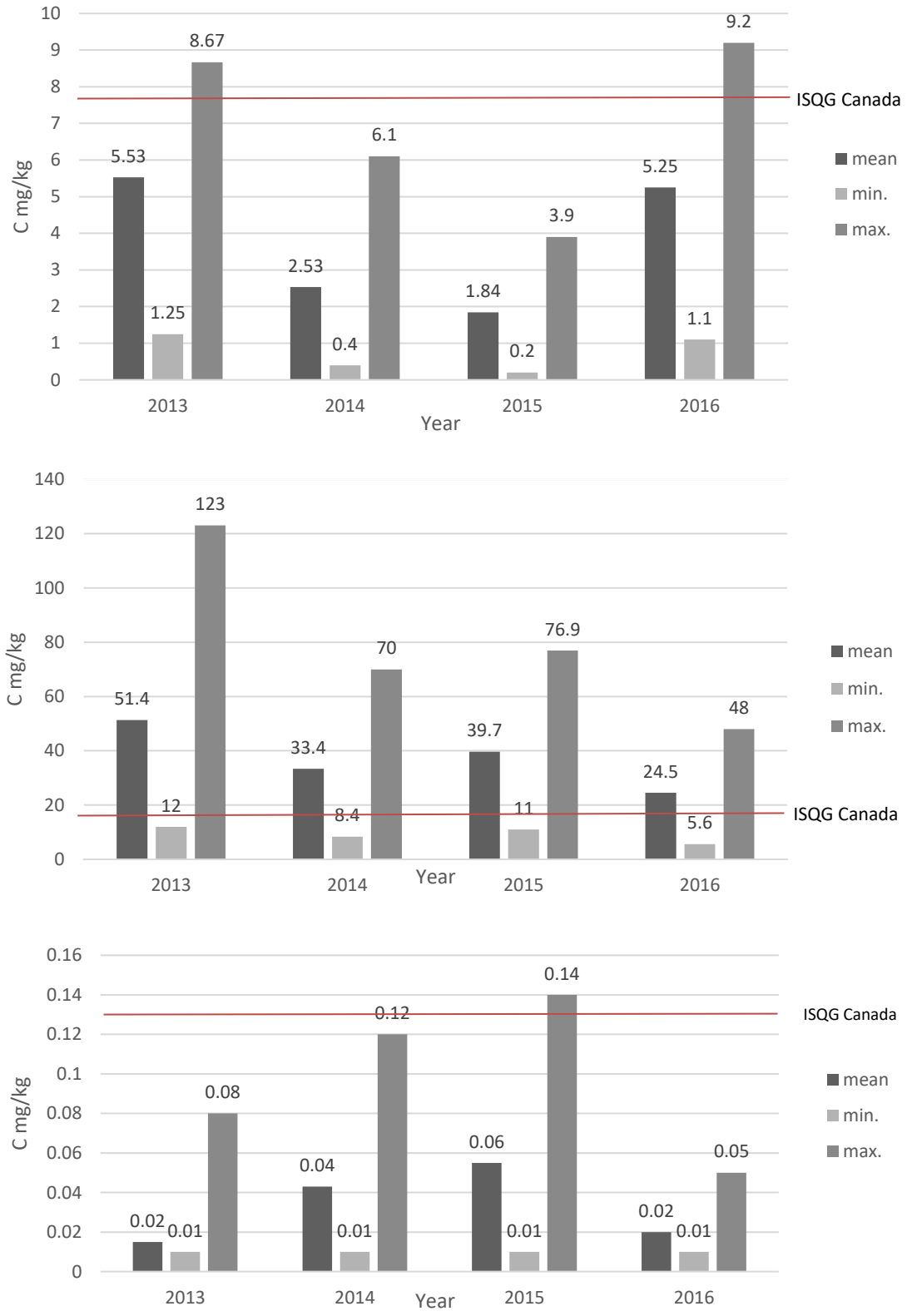

Figure 3. POAL: Arsenic, copper and mercury concentrations (mg/kg) in sediments 2013-2016 and Canadian quality guideline value (POAL, 2017)

As shown in the figure 3, the maximum concentration of arsenic in 2013 and 2016 exceed the Canadian Sediment Quality Guidelines (7.24 mg/kg). However, the maximum concentrations are four times smaller than Canadian PEL (probable effect level), which is 41.6 mg/kg for arsenic.

The maximum and mean concentration of copper in 2013-2016 as well exceed the Canadian Sediment Quality Guideline (18.7 mg/kg). PEL value for copper is 108 mg/kg, which was exceeded in 2013.

The average mercury concentration does not exceed the quality line and therefore does not pose a significant risk to the aquatic ecosystem. In some of the sampling points, mercury concentrations did not exceed the detection limit (0.01).

5.2 Ecological risk analysis in the communes of Concón, Quintero and Puchuncaví

The Ministry of the Environment has requested an ecosystem study in the commune of Quintero, Concón and Puchuncaví, under the name of "Ecological risk analysis by potentially polluting substances in air, soil and water, in the communes of Concón, Quintero and Puchuncaví." The general objective of the study was to characterize the environmental compartments of water, sediment and biota in the Quintero Bay (CEA, 2013).

The Center of Environmental studies (CEA) applied a study in the winter season in June 2012 and in the summer season in January 2013 to meet the specific objectives of the ecosystem study. It characterizes the components of water, sediment and biota of the Quintero Bay. Six sampling points were used for the sediment analysis, which two of them were same as used in the monitoring of the Coastal Environment Observation Program (POAL).

The results of sediment quality both in winter and summer studies are presented below. There is no national standard with which to compare the sediment values. For this reason, the levels defined in the guidelines for the protection and management of the quality of aquatic sediments of Canada was used as reference.

All of the metals analyzed, beryllium, silver and selenium were found to be below the detection limit at all sampling points during both monitoring campaigns. Alumnium, barium, boron, cobalt, iron, manganese, molybdenum, nickel and vanadium were analyzed, but because these trace metals pose a little threat to the aquatic environment and there is no Canadian ISQG value for those metals, the comparison cannot be made so the results are not presented. Arsenic, chromium, copper and mercury concentrations in the sediments in both periods (summer, winter) are presented in figure 4.

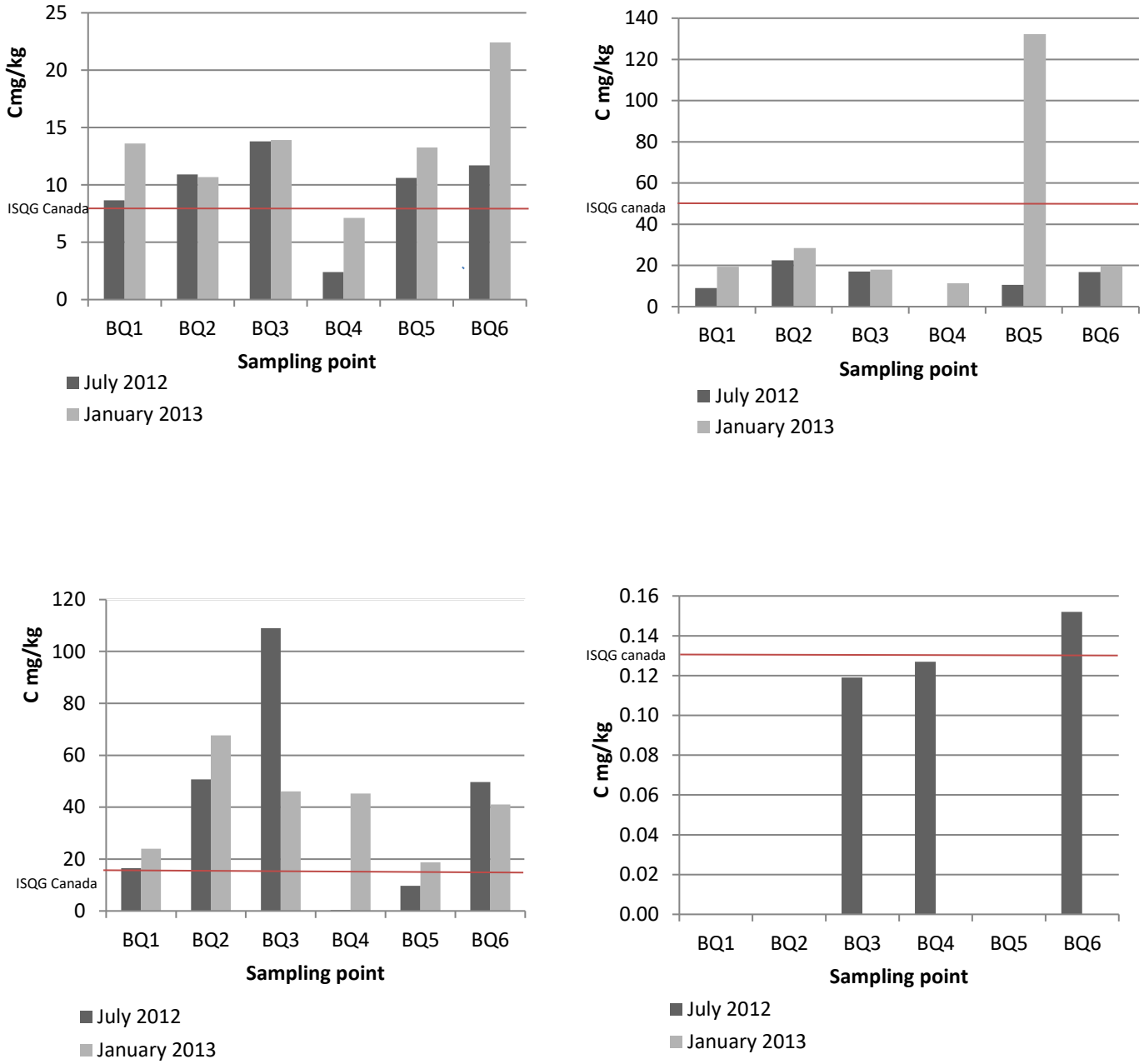

Figure 4. CEA: arsenic, chromium, copper and mercury concentration for six sampling points in winter 2012 and summer 2013 in Quintero Bay (CEA, 2013)

In the winter season, arsenic concentrations varied between below detection limit and 13.80 mg/kg, having an average concentration of 11.13 ± 1.86 mg/kg throughout the study area. The summer season meanwhile, recorded concentrations between 7.11 and 22.41 mg/kg, while the average concentration was 13.49 ± 5.07 mg/kg. Canadian ISQG value for arsenic is 7.24 mg/kg.

During the winter season, chromium concentrations varied between value below the detection limit and 22.50 mg/kg. The study area averaged 15.21 ± 5.44 mg/kg. During the summer season, the concentrations of chromium fluctuated between 11.31 and 132.20 mg/kg. However, the exceptionally high value in in sampling point BQ5 might indicate to an error in the analysis. Canadian ISQG value for chromium is 52.3 mg/kg.

The study area had an average copper concentration 47.1 ± 39.3 mg/kg during the winter season, with a minimum below the detection limit (<0.3 mg/kg) and maximum of 109.0 mg/kg. In the summer season, the average concentration was 40.5 ± 17.5 mg/kg, with a minimum content of 18.8 mg /kg and a maximum of 67.7 mg/kg. Canadian ISQG value for copper is 18.7 mg/kg.

During the winter season, the average mercury concentration was 0.13 ± 0.01 mg/kg. Sampling points BQ1, BQ2 and BQ5 recorded values below the detection limit (<0.1 mg/kg), while point BQ6 had the highest concentration, with 0.15 mg/kg. In the summer season, all sampling points recorded concentrations below the detection limit (<0.1 mg/kg). The Canadian sediment quality guideline for mercury is 0.13 mg/kg.

During the winter season, cadmium had an average concentration of 0.20 ± 0.17 mg /kg in the study area, with a minimum value below the detection limit and a maximum of 0.39 mg/kg. During the summer season, all the six sampling points were below the detection limit. Canadian ISQG value for cadmium is 0.7 mg/kg.

In winter season, an average lead concentration was 6.86 ± 4.13 mg/kg, and in the summer season, the study area averaged 10.53 ± 4.12 mg/kg. The Canadian sediment quality guideline for lead is 30.2 mg/kg.

5.3 The impacts of the hydrocarbon spill in affected area of Quintero Bay

In 2015, after the three significant oil spill accidents in the Quintero Bay, The Fisheries Development Institute (IFOP) developed a project related to the impacts of the hydrocarbon spill in the affected area. The objective of this study was to determine impacts on hydrobiological species, marine ecosystems and socioeconomic aspects of communities associated with fishing activities in the hydrocarbon spill affected area in the Quintero Bay, V Region. One part of the large study was to determine the current status of the presence of the chemicals in the water column and the sediments and to compare this information with the existing historical information of the Quintero Bay (IFOP, 2016).

Two sampling campaigns were carried out, first in August / September 2015, corresponding to the winter condition, and the other during January / February 2016, corresponding to the summer condition. For the metal determinations a total of 543 samples were obtained, of which 144 were sediment samples and 399 biota. The content of the following heavy metals was determined: arsenic, cadmium, copper, nickel, lead, vanadium and zinc.

Table 7 shows the mean values and standard deviation of total cadmium, total copper, total lead and total zinc concentrations of subtidal sediments in the Quintero Bay and the control point located in the northern Cachagua sector, about 21 kilometers away from the intermediate point of the Bay. The control point was used as a reference, for being an area that has expected to have less anthropogenic intervention in the marine systems than in the Quintero Bay. Again, in this study the levels defined in the guidelines for the protection and management of the quality of aquatic sediments of Canada was used as reference, because there is no national standard with which to compare the sediment values.

Table 7. *Average concentration (mg / kg) and standard deviation of heavy metals in sediments in three zones of the Quintero Bay and control zone (Cachagua) in 2015 (IFOP, 2016).*

Parameter	**Area**	**Number of samples**	**Average (mg/kg)**	**SD**
Cadmium Total	B	3	0.100	0.000
Cadmium Total	C	2	0.100	0.000
Cadmium Total	D	5	0.100	0.000
Copper Total	B	3	25.700	19.883
Copper Total	C	2	37.933	13.105
Copper Total	D	5	15.000	4.504
Lead Total	B	3	4.611	1.971
Lead Total	C	2	7.150	0.542
Lead Total	D	5	4.940	2.522
Zinc Total	B	3	20.922	1.597
Zinc Total	C	2	20.000	0.000
Zinc Total	D	5	20.000	0.000
Cadmium Total	Control	3	0.100	0.000
Copper Total	Control	3	10.000	0.000
Lead Total	Control	3	3.467	0.577
Zinc Total	Control	3	20.000	0.000

When comparing the results between the control point and the Quintero Bay, it can be observed that the concentrations of the total copper and lead are higher, especially in the zone C. Taking into account any of the reference or control values, the Quinter Bay is most likely slightly polluted due to the industrial use of the coastal edge.

The Canadian sediment quality guideline (ISQG) value for copper is 18.7 mg/kg, which lead to the assumption that the Quintero Bay is moderately contaminated by copper. However, the PEL (probable effect level) is 108 mg/kg. The lower value (ISQG) represents the concentration where the harmful biological effects are expected to occur rarely. The

upper value (PEL) represents the level where the adverse effects are expected to occur more frequently. ISQG value for lead is 30.2 mg/kg, which means that the area is not significantly contaminated by lead, although concentrations are a bit higher than in the control area.

5.4 Distribution and pollution assessment of trace elements in the Quintero Bay

The fourth source of information is related to the results of the work of Parra et al (2015) published in the Marine Pollution Bulletin. The main objective of this study was to assess the levels of heavy metal pollution in the clay/silt fraction (<63 μm fraction) of marine sediments from Quintero Bay, Chile. For this, sediment samples were collected from 14 sampling points, located in the Quintero bay, and analyzed for major and minor element determination. Concentrations of Cu, Se, Mo, As, Sb and Pb were found suggest an anthropogenic origin. The concentrations of Cu, Zn, As and Pb are most likely associated with by the copper smelter (Parra et al., 2015).

Table 8. *Range of heavy metal concentrations (mg/kg) in surface sediments of Quintero Bay determined by ICP-MS (Parra et al., 2015)*

Metal	**As**	**Cu**	**Cr**	**Pb**	**Zn**
C mg/kg	9*-20**	41-1476	27-80	17-36	65-167
control site	9	41	27	15	65
ISQG Canada	7.24	18.7	52.3	30.2	124

*min, **max concentration found

The reported values concentrations of five heavy metals found in the bay are presented in the table 8. There is a big variation in the concentrations, especially in copper concentrations, varying from 41 g/kg up to 1476 mg/kg dry weight.

However, the study does not specify the date of the sampling, and the sampling sites were different than the POAL have used. Besides, the concentrations obtained in this study are significantly higher than other information, which could be attributed to differences in the analytical technique used. For these reasons this information was considered only for reference purposes.

5.5 Summary of the previous studies

Almost all of the results of the previous studies indicate that all metal concentrations, except arsenic and copper, fell within the lower end of the Sediment Quality Guideline Range. This would signify that those metals from the sediments do not pose a significant threat to the organisms in the system.

According to the previous studies, moderately high concentrations of copper and arsenic were found from the Quintero Bay, especially in the study of Parra et al. (2005). The results of arsenic and copper from four different studies shown in the previous chapter are summarized in the table 9.

Table 9. *Range of arsenic and copper concentrations in 2013 and 2015 from four studies in Quintero Bay*

Study	**Arsenic (mg/kg)**	**Copper (mg/kg)**
CEA, 2013 (summer)	7.11-22.41	18.8-67.7
POAL, 2013	1.25-8.67	12-123
POAL, 2015	0.2-3.9	11-76.9
IFOP, 2015	*Not recorded*	15-37.9
Parra et al., 2015	9-20	41-1476
ISQG Canada	**7.24**	**18.7**

The study area is not significantly affected by arsenic, because no arsenic concentrations exceeded PEL values (41.6 mg/kg). However, average concentrations of arsenic in two studies (Parra et al., CEA) exceeded the ISQG value. Thus, at concentrations of arsenic in sediments greater than the ISQG, toxic effects from long-term exposure to arsenic might occur. When exposed to levels greater than ISQG values, effects may be observed in some sensitive species, whereas the upper PEL value is likely to cause harmful effects in a wider range of organisms.

However, these studies are mainly focused on total arsenic concentrations whereas less attention has been paid to different arsenic fractions. For example, arsenite is much more mobile and toxic than arsenate, so each arsenic fraction might have different bioavailability depending on the different ratio of arsenite or arsenate.

Table 10 illustrates comparison between arsenic concentration found in the Quintero Bay and worldwide. The arsenic concentrations in the Quintero Bay are similar to those found in Gulf of Finland (Vallius et al., 2007).

Table 10. *Range of arsenic concentration in the sediments in Quintero Bay, Arabian Gulf, Tupinambá Brazil and Gulf of Finland*

Location	**As (mg/kg)**	**Reference**
Quintero Bay, Chile	7.11-22.41	CEA, 2013
Quintero Bay, Chile	1.25-8.67	POAL, 2013
Tarut Island, Arabian Gulf	53-342	El-Sorogy et al., 2015
Tupinambás, São Paulo, Brazil	13-23	Hoff et al., 2014
Gulf of Finland	7.25-19.1	Vallius et al., 2007

The Canadian sediment quality guideline (ISQG) value for copper is 18.7 mg/kg, which lead to the assumption that the Quintero Bay may be moderately contaminated by copper. The PEL (probable effect level) for copper is 108 mg/kg. All of the studies except Parra et al. showed copper concentrations below this upper PEL value, where the adverse effects are expected to occur more frequently. The upper PEL value is likely to cause harmful effects in a wider range of organisms.

Table 11 illustrates comparison between Cu concentration in the Quintero Bay and worldwide. Again, the copper concentrations in the Quintero Bay are similar to those found in Gulf of Finland (Vallius et al., 2007).

Table 11. *Copper concentration in the sediments in Quintero Bay, North Persian gulf, Gulf of Finland and Quinzhou bay, China*

Location	**Cu (mg/kg)**	**Reference**
Quintero Bay, Chile	18.8-67.7	CEA, 2013
Quintero Bay, Chile	11-76.9	POAL, 2015
Northwest Persian gulf, Iran	17.9-47.9	Pejman et al., 2015
Gulf of Finland	42.1-76.3	Vallius et al., 2007
Qinzhou bay, China	1.89–43.45	Gu et al., 2015

The different studies made in Quintero Bay are summarized and compared in the table 12.

Table 12. *Comparison of different studies (CEA, IFOP, POAL, PARRA)*

Study	Parameter	Sampling points	Study method	Frequency	Sampling area
CEA	Metals, total concentrations	6	*Not specified*	2 sampling periods (summer, winter 2012-2013)	Surface sediments
POAL	metals, total concentrations	14	Acid digestion+ FLAA/ICP-AES or GFAA/ICP-MS	Once a year	Surface sediments (first 5 cm)
IFOP	Metals, total concentrations	3 zones	Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES/ICP-MS Analysis)	2 sampling periods, winter 2015 and summer 2016	Surface sediments
Parra et al.	Metals, total concentrations	14	ICP-AES/ICP-MS	2015	Surface sediment samples (500g)

In all of the presented studies, total concentrations of heavy metals were measured with similar study methods. Specific determination method of heavy metal concentrations was not presented in the final report of ministry of the environment (CEA), however, it is expected to be similar with the other studies. All of the studies used surface sediment samples. This first layer accumulate the substances of the recent years and thus is suitable for evaluating the current situation.

All of the presented studies have measured the total metal concentrations that may offer valuable information about contamination levels, but in some cases the total concentration is not always a sufficient measure of environmental impact of the polluted sediments, hence the behavior of the metals in the environment depends on their binding states, and specific forms (e.g. oxides, metal carbonates, sulfides, organometallic compounds, etc.) (Gao & Chen, 2012).

6. RECOMMENDATIONS FOR THE SEDIMENT MONITORING PROGRAM AND FUTURE DIRECTIONS

The concentrations of several heavy metals in the sediments were found at the area of the Quintero Bay. Therefore, it is important to monitor and evaluate the possible impacts of heavy metals in the sediments. The objectives of the long-term or temporal monitoring plan usually include the data collection, evaluation of the physical and chemical sediment characteristics and evaluation of the changes over time. Sediment quality is assessed by comparing measured results to historical values to identify any changes that have occurred. It is also preferred to have a control area, which can be used as a reference, for being an area that has expected to have less anthropogenic intervention in the marine systems.

The practical part and suggestions for the sediment monitoring objectives for the Quintero Bay are presented in this chapter.

6.1 Sediment monitoring objectives

Sediment management strategy include evaluation of the changes over time to the physical as well as chemical characteristics of the sediments at long-term monitoring stations and to provide data for researchers and managers. Sediment monitoring in practice usually consist of following steps: sample collection including field measurements, sample treatment and finally, evaluating the collected data.

Sample collection for physical and chemical sediment characteristics should be performed at several (approx. 8-12) long-term monitoring stations chosen from different geographic locations throughout Quintero Bay. Sediments collected for chemical analyses should be removed from the top surface layer only (2-3 cm), because trend monitoring requires information about the current pollutants burden in the upper sediment layer and this first layer accumulate the trace metals of the recent years. Only if long-term time series (decades/centuries) are part of the research, the deeper sediment layers should be analyzed (HELCOM, 2017). Sediment samples should be deep frozen as soon as possible after packing in order to avoid loss in trace metal samples (especially mercury). Once frozen, the samples can be stored at temperatures of –20ºC or below. In addition, all sample collection and analysis methods must be held consistent between years (HELCOM, 2017).

Measurements of sediment penetration depth, temperature, salinity of the water overlying the sediment surface, and sediment texture, color and odor are taken by ecology personnel

in the field during sample collection. Sediment monitoring programs should also include the basic physicochemical properties of the sediments (organic carbon, grain size etc.) (EU, 2010).

The indicators considered for sediment monitoring program should include all the heavy metals and polycyclic aromatic hydrocarbon (PAH), as recommended in the water frame work directive (EU, 2010). Evaluation should be based on the guidelines established in the corresponding legislation. However, if this legislation is not available, like in Chile, it is advisable to evaluate the results with some of the existing EQS, for example Canadian environmental guidelines, before the establishment of the corresponding legislation.

Heavy metals usually appear in sediments in low concentrations. Instrumental determination of heavy metals is carried out depending on the manufacturer's specifications and instrument. In most cases, i.e., in most marine sediments, cadmium and lead can be determined by GFAAS (Graphite Furnace Atomic Absorption), while copper, zinc, chromium, nickel, aluminum and iron can be determined by flame atomization (HELCOM, 2017). The laboratories conducting the chemical and toxicity analyses must use the same procedures from year to year, or explain any procedure they wish to change, and provide evidence that procedural changes do not render the data incomparable.

6.2 Further studies

Several studies of contaminated sediments has been carried out. However, these studies are mainly focused on total metal concentrations whereas less attention has been paid to the speciation in different metal fractions. Although the total concentration of heavy metals in sediments can offer valuable information of the sediment contamination, it is not always a good indication of the bioavailable metals, which can directly affect aquatic organisms (Gorski et al., 2008). For example, arsenite is much more mobile and toxic than arsenate, so each arsenic fraction might have different bioavailability depending on the different ratio of arsenite or arsenate. The aims of future work, therefore, are to asses both total concentration of heavy metals, and also the chemical forms in which they occur.

In addition, sediment toxicity and benthic index has not been measured. The proper use of different sediment quality assessment tools will provide the most serviceable information, because it is widely known that a single tool should not be used to predict if adverse biological effects will occur or not. Annual collection of benthos must occur at the same time of year, so that the population is in similar growth and reproductive condition.

Due to the existing industrial development, as well as the constant transport of hydrocarbons and other substances, the Quintero Bay presents a constant risk of contamination which can affect the rest of activities that take place in the coastal edge. During the last 10 years, 10 spill events have been reported, which have had different environmental and

social implications. Therefore, studies about the effects of hydrocarbons should be performed in addition to the heavy metal studies.

In recent years, there have been some remediation efforts in the Quintero bay. For example, FIC Algas developed a study with the University of Andrés, where the bioaccumulation capacity of heavy metals and organic compounds in cultivated macroalgae was determined. The giant kelp was cultivated 120 days in three different locations (Ventanas, Horcon and Maitencillo) close to the Quintero Bay. The study showed that during the cultivation time (120 days) giant kelp was able to grow normally in the area and there were no differences in their productive parameters in the three different locations. The growth rate, accumulated biomass and crop productivity fluctuated in similar ranges, without clear evidence of problems or disadvantages in the cultivation. The constant fluctuation of metal concentrations in the algae tissue was observed during the 120 days of cultivation. For example, a greater concentration of arsenic was found in all three sampling sites (FIC Algas, 2016). Therefore, bioremediation could be an efficient and cheap method for remediation and similar studies should be preferred.

7. CONCLUSIONS

The concentrations of several heavy metals in the sediments were found at the estuarine area of the Quintero Bay. Based on the Canadian SQGs, arsenic and copper will most likely cause adverse biological effects. The origin of these concentrations can be attributed to the industrial development that exists in the Quintero Bay. Therefore, it is important to monitor heavy metal concentrations in the future. Suitable sediment management strategy could be to evaluate changes over time to the chemical and physical characteristics of the sediments at long-term monitoring stations. The suitable monitoring frequency of chosen priority substances could be once a year, as in the annual sediment analysis of the Environmental Monitoring Program POAL.

However, potential effects of arsenic and other trace metals cannot only be determined by measuring their total concentrations due to their different bioavailabilities. All of the studies have measured the total heavy metal concentrations that may offer valuable information about contamination levels, but total concentration is not always a sufficient measure of environmental impact of the polluted sediments, hence the behavior of the metals in the environment depends on their binding states, and specific forms. The aims of future work, therefore, are to asses both total concentration of heavy metals, and also the chemical forms in which they occur. In addition, the toxicity and benthic index measurements should be performed in the Quintero Bay, because the use of different sediment quality assessment methods will provide the most useful information.

The physical, chemical, and biological factors complicate the application of the sediment management tools and introduce uncertainty. The environment is heterogeneous and dynamic, and the physical and chemical properties of the sediments might vary within one study area. Organisms' exposures to pollutants in the sediments may occur by several routes, such as via ingestion or direct contact. In addition, sediment contamination is usually a complex mixture of compounds whose interactions are not well known and bioavailability can be difficult to predict. Therefore, sediment quality guidelines based on laboratory toxicity bioassays may not always be environmentally relevant. For example, in situ investigation should be encouraged and may compensate this limitation. For this purpose, both acute and chronic toxicity tests may be developed, for example, through bioassays such as LC_{50} (medium lethal concentration) and EC_{50} (medium effective concentration), among others, to help understand the effects and risks of presence of these metals in the ecosystem.

Sediment quality guidelines work anyway as a simple and time-effective method to assess the overall sediment quality and they provide scientific tools for evaluating the possible adverse biological effects in aquatic environments. They can also serve as benchmarks

for discussions on emission reductions, in environmental impact evaluation and for sediment quality monitoring programs. Evaluation of the sediment quality should be based on these guidelines established in the corresponding legislation. However, since the legislation is not available in Chile, it is advisable to evaluate the results with some of the existing EQS, in order to get a roughly idea of the current sediment status. The existing guidelines can also be used to help the progress of any future environmental legislation and sediment monitoring program in Chile.

Since the heavy metals, especially arsenic and copper, might cause adverse biological effects, some sediment remediation actions should be taken into consideration. Bioremediation could be an efficient and cheap method for remediation, and recent studies with giant kelp have shown good signs. In addition, bioremediation is a good alternative in those cases, when the remediation process might be worse than the original situation—e.g., when remediation techniques, such as dredging, cause more damage to the environment than leaving the sediment in place. Therefore, similar actions should be encouraged in order to improve better ecological status of the Quintero Bay.

REFERENCES

Ahlf, W., Hollert, H., Neumann-Hensel, H., Ricking, M., (2002). A guidance for the assessment and evaluation of sediment quality: a German approach based on ecotoxicological and chemical measurements. Journal of Soils and Sediments (online first)

Anan Y., Kunito T., Tanabe S., Mitrofanov I., Aubrey D.G., (2005). Trace element accumulation in fishes collected from coastal waters of the Caspian Sea. Mar. pollut. bull., 51(8–12): 882–888.

ATSDR Agency for Toxic Substances and Disease Registry, (1999). Public health service. Atlanta: U.S. department of health and human services; 1999. Toxicological profile for lead

Benjamin M.M, Honeyman B.D., (1992). Trace metals, London

Bissen M., Frimmel F.H., (2003). Arsenic – a review. Part I: occurrence, toxicity, speciation and mobility. Acta hydrochim hydrobiol, 31: 9–18.

Botté S.E., Freije R.H., Marcovecchio J.E., (2010). Distribution of several heavy metals in tidal flats sediments within Bahia Blanca estuary

Brils J., (2008). Sediment monitoring and the European Water Framework Directive Ann Ist super s AnItà 2008 Vol. 44, no. 3: 218-223

Bryan, G.W., (1976). Some aspects of heavy metal tolerance in aquatic organisms. In A.P.M Lockwood (Ed): Effects of pollutants on aquatic organisms. Cambridge University press, Cambridge. Pp 7-34

Bryan G.W, Langston W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ. pollut. 76, 89-131

Burkhard L.P., Cook P.M., Lukasewycz M.T., (2005). Comparison of biota-sediment accumulation factors across ecosystems. Environmental science & technology 39:5716-5721.

Carpentier S., Moilleron R, Beltrán C., Hervé D., Thévenot D., (2002). Quality of dredged material in the river Seine basin (France), Science of the total environment, 295, 101–113.

CCME Canadian Council of Ministers of the Environment, (1999). Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life. CCME EPC-98.

CCREM Canadian Council of Resource and Environment Ministers, (1987). Canadian water quality guidelines. Prepared by the task force on water quality guidelines.

CEA the center of environmental studies, Chile (2013). Análisis de riesgo ecológico por sustancias potencialmente contaminantes en el aire, suelo y agua en las comunas de Concón, Quintero y Puchuncaví

Chapman P.M., Allen H.E., Z'Graggen M.N., (1996). Evaluation of bioaccumulation factors in regulating metals. Environmental science and technology journal, 30, 448A-452A.

Chiarelli R., Roccheri M., (2014). Marine invertebrates as bioindicators of heavy metal pollution. Open journal of metal, 4, 93-106.

Chilean maritime autor, (2014). Investigación elevó a 38 mil litros el derrame de petróleo en Quintero available: (referred 5.12.2014) http://www.cooperativa.cl/noticias/pais/medioambiente/contaminacion/investigacion-elevo-a-38-mil-litros-el-derrame-de-petroleo-en-quintero/2014-12-05/133405.html

Ciliberti A., Berny P., Delignette-Muller M.L., Buffrénil V., (2011). The Nile monitor (Varanus niloticus; Squamata: Varanidae) as a sentinel species for lead and cadmium contamination in sub-Saharan wetlands. Science of the total environment 2011; 409:4735–45.

Codelco annual sustainability report (2015). Available (referred 13.07.2017): https://www.codelco.com/memoria2015/pdf/reporte-sustentabilidad/en/codelco-sustainability-report-2015.pdf

Crane, M., Everts J., Van de Guchte K., Heimbach F., Hill I., Matthiessen P., Stronkhorst J., (1996). Research needs in sediment bioassay and toxicity testing. In: Munawar.

Cullen W.R., Reimer K.J., (1989). Arsenic speciation in the environment. Chemical reviews 89, 713–764.

Dafforn K.A, Lewis J.A., Johnston E.L., (2011). Antifouling strategies: history and regulation, ecological impacts and mitigation Mar. pollut. bull., 62 (2011), pp. 453-465.

DS 90/2000 Decreto Supremo 90: manual de aplicación ministerio secretaría general de la presidencia de la república. Available (referred 23.07.2017): http://www.leyesambientales.cl/riles_en/manual_ds_90_00.pdf

Demars K.R., Richardson G.N., Yong R.N., Chaney R.C., (1995). Dredging, remediation, and containment of contaminated sediments, ASTM International, 1995 - 333 pages.

Duarte B., Caetano M., Almeida P.R, Vale C., Cacador I., (2010). Accumulation and biological cycling of heavy metal in four salt marsh species from Tagus estuary, Portugal.

Duffus J.H., (2002). Heavy metals: a meaningless term? Pure appl. chem. 2002;74(5):793–807.

EEA European Environmental Agency, (2003). Hazardous substances in marine organisms and loads to coastal waters: cadmium, EEA Report 2/2003, European Environment Agency.

EEA/UNEP European Environment Agency and United Nations Environment Programme (1999). Chemicals in the European Environment: low doses, high stakes? The EEA and UNEP annual message 2 on the state of Europe's environment.

El-Sorogy A.S., Youssef M., Al-Kahtany K., Al-Otaiby N., (2015). Assessment of arsenic in coastal sediments, seawaters and molluscs in the Tarut Island, Arabian Gulf, Saudi Arabia, Journal of african earth sciences 113 (2016) 65-72.

EMSA: European maritime safety agency, (2012). Addressing illegal discharges in the marine environment. Available: http://www.emsa.europa.eu/damage-stability-study/items.html?cid=77&id=1879

ENAP annual report (2015). available (referred 17.7.2017): https://www.enap.cl/pag/586/1678/

European Union, (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy (Water Framework Directive).

EU (2010): Common implementation strategy for the Water Framework Directive (2000/60/EC): Technical report - 2010 – 041 Guidance document No. 25 on chemical monitoring of the sediment and biota under the water framework directive. available: https://circabc.europa.eu/sd/a/7f47ccd9-ce47-4f4a-b4f0-cc61db518b1c/Guidance%20No%2025%20-%20Chemical%20Monitoring%20of%20Sediment%20and%20Biota.pdf

Ferguson J.E., Gavis J., (1972). A review of the arsenic cycle in natural waters. Water res. 6:1259-1274.

Fergusson J. E., (1990). The heavy elements: chemistry, environmental impact, and health effects. Pergamon press, 1990 - 614 pages.

FIC Algas, (2016). Cultivo del alga parda *Macrocystis pyrifer* en la zona de Quintero y Puchuncavi: evaluación de la productividad y potencial uso para bioremediacion de metales pesados y compuestos organicos. Universidad Andrés.

Franson J.C., Pain D.J., (2011). Lead in birds. In: Beyer W.N., Meador J.P. (eds) Environmental contaminants in biota: interpreting tissue concentrations. CRC Press, Boca raton, pp 563–593.

Gao X., Chen C.T., (2012). Heavy metal pollution status in surface sediments of the coastal Bohai Bay. Water res. 2012 Apr 15;46(6):1901-11.

GIPME, Global Investigation of Pollution in the Marine Environment, (2000). Guidance on assessment of sediment quality. London, UK: International Maritime Organization.

Govind P., Madhuri S., (2014). Heavy metals causing toxicity in animals and fishes, review paper, research journal of animal, veterinary and fishery sciences.

Gorski P.R., Armstrong D.E., Hurley J.P., Krabbenhoft D.P., (2008). Influence of natural dissolved organic carbon on the bioavailability of mercury to a freshwater alga. Environ. pollut.,154,116-123.

Goyer, (1997). Toxic and essential metal interactions; annual reviews of nutrition, 1997, 17, 37-50.

Graeme, K.A., Pollack, C.V., (1998). Heavy metal toxicity, part I: arsenic and mercury. The journal of emergency medicine, 16, 45-56.

Gu, Yang-Guang, Lin, Qin, Yu, Zi-Ling, Wang, Xu-Nuo, Ke, Chang-liang, Ning, Jia-Jia, (2015). Speciation and risk of heavy metals in sediments and human health implications of heavy metals in edible nekton in Beibu Gulf, China: A case study of Qinzhou Bay. Marine pollution bulletin. 10.1016/j.marpolbul.2015.11.019.

Haileslassie T., Gebremedhin K., (2015). Hazards of heavy metal contamination in ground water. Available: http://www.ijteee.org/final-print/feb2015/Hazards-Of-Heavy-Metal-Contamination-In-Ground-Water.pdf

Heath A.G., (1987). Water pollution and fish physiology. CRC press, Florida, 245 pp.

HELCOM (2017). Manual for Marine Monitoring in the COMBINE program of HELCOM, Annex B-13 Technical note on the determination of heavy metals and persistent organic compounds in marine sediments available: http://helcom.fi/Documents/Action%20areas/Monitoring%20and%20assessment/Manuals%20and%20Guidelines/Manual%20for%20Marine%20Monitoring%20in%20the%20COMBINE%20Programme%20of%20HELCOM.pdf

Hoff N., Figueira R., Abessa D., (2014). Levels of metals, arsenic and phosphorus in sediments from two sectors of a Brazilian marine protected area (Tupinambás ecological station). November 2014, Marine pollution bulletin DOI: 10.1016/j.marpolbul.2014.10.044

Holleman A.F., Wiberg E., Wiberg N., (1985). "Cadmium". Lehrbuch der anorganischen chemie, 91–100 (in German). Walter de Gruyter. pp. 1056–1057.

Ingresoll C.G., Ankley G.T., Baudo R., Burton G.A., Lick W., Luoma S., MacDonald D.D., Reynoldson T.B., Solomon K.R., Swartz R.C., Warren-Hicks W.J., (1997). Work group summary report on uncertainty evaluation of measurement endpoints used in sediment ecological risk assessment. In: Ingersoll C.G., Dillon T., Biddinger G.R., editors. Ecological risk assessment of contaminated sediment. Pensacola FL: SETAC Press. p 297-352.

IFOP: Instituto de fomento pesquero, (2016). INFORME FINAL "Determinación de los impactos en los recursos hidrobiológicos y en los ecosistemas marinos presentes en el área de influencia del derrame de hidrocarburo de Bahía Quintero, V Región.

ICSUNIDO: International Centre for Science and High Technology, (2007). Survey of sediment remediation technologies. Trieste, Italy. Available: https://clu-in.org/download/contaminantfocus/sediments/Survey-of-sediment-remediation-tech.pdf

Ip C.C.M., Li X.D., Zhang G., Wai O.W.H., Li Y.S., (2007). Trace metal distribution in sediments of the Pearl River estuary and the surrounding coastal area, South China. Env. poll. 147: 311-323.

Jersak J., Göransson G., Ohlsson Y., Larsson L., Flyhammar P., Lindh P., (2016). In-situ capping of contaminated sediments. Sediment remediation technologies: a general overview. SGI Publication 30-3E, Swedish Geotechnical Institute, SGI, Linköping.

Järup L., Åkesson A., (2009). Current status of cadmium as an environmental health problem. Toxicology and applied pharmacology 2009; 238:201–8.

Karlsson J., Ytreberg E., Eklund B., (2010). Toxicity of anti-fouling paints for use on ships and leisure boats to non-target organisms representing three trophic levels Environ. Pollut. 158, pp. 681-687.

Langston W.I., (1990). Toxic effects of metals and the incidence of marine ecosystems, n: Furness R.W., Rainbow P.S., editors. Heavy metals in the marine environment. CRC Press, New York 256 pp.

Long E.R., Chapman P.M., (1985). A sediment quality triad: measures of sediment contamination, toxicity and infaunal community composition in Puget Sound. Marine pollution bulletin volume 16, Issue 10, October 1985, Pages 405-415.

Long E.R., MacDonald D.D., Smith L., Calder F.D., (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental management 19: 81-97.

Luoma S.N., Carter J.L., (1993). Understanding the toxicity of contaminants in sediments: beyond the bioassay-based paradigm. Environ. toxicol. chem. 12:793–796.

Mance G., Brown V. M., Yates J., (1984). Proposed environmental quality standards for list II substances in water – copper. Water research centre technical report, water resource centre, Buckinghamshire, UK.

Markert B., Wappelhorst O.,Weckert V., Herpin U., Siewers U., Friese K., Breulmann, G., (1999). The use of bioindicators for biomonitoring the heavy-metals status of the environment. J. Radioanal. Nuclear chem., 240(2):425-429.

Monteiro S.M., Santos N.M., Calejo M., Fontaínhas-Fernandes A.A., Sousa M., (2009). Copper toxicity in gills of the teleost fish, Oreochromis niloticus: effects in apoptosis induction and cell proliferation. Aquat. toxicol. 94:219-228.

Morillo J., Usero J., Rojas R., (2008). Fractionation of metals and As in sediments from a biosphere reserve (Odiel salt marshes) affected by acidic mine drainage. Environ monit assess.

Neff, J.M., (1997). Ecotoxicology of arsenic in the marine environment (review). Environ.toxicol. chem. 16, 917.

Neff, J.M., (2002). Arsenic in the ocean. In: bioaccumulation in marine organisms effect of contaminants from oil well produced water. Elsevier science, Oxford, pp. 57e78.

Nor Y.N., (1987). Ecotoxicity of copper to aquatic biota: a review. Environ. res. 43:247-282.

Oehlmann J., Schulte-Oehlmann U., (2003). Endocrine disruption in invertebrates. Pure appl. Chem. 75:2207-2218.

OSPAR, (1996). 'Ecotoxicological assessment criteria. Report of the third workshop, the Hague 25– 29 November 1996.

OSPAR, (2010). Quality status report 2010: assessment of the impact of shipping on the marine environment (2010).

Paredes M.T., (1998). Determinación de metales pesados en dos especies de Bivalvos del estuario de Valdivia y la Bahía de Corral (X región) mediante análisis electrotérmico. Tesis, Escuela de Biología Marina, Facultad de Ciencias, Universidad Austral de Chile, 52 pp.

Parra S., Bravo M.A., Quiroz W., Querol X., Paipa C., (2015). Distribution and pollution assessment of trace elements in marine sediments in the Quintero Bay (Chile). Mar pollut. bull. 2015 Oct 15;99(1-2):256-63.

Pejman, A., Bidhendi, G.N., Ardestani M., Saeedi M., Baghvand A., (2015). A new index for assessing heavy metals contamination in sediments: a case study. Ecological indicators, 58, 365-373.

Plant J.A., Korre A., Reeder S., Smith B., Voulvoulis N., (2005). Chemicals in the environment: implications for global sustainability. Appl. earth sci. (trans. inst. min. metall. B). 2005; 114(B65): 1–33.

POAL: Programa de observación del ambiente litoral (2017). Available (referred 20.10.2017): https://www.directemar.cl/directemar/site/edic/base/port/poal.html

Pourabadehei M., Mulligan C.N., (2016). Resuspension of sediment, a new approach for remediation of contaminated sediment. Environ pollut. 2016 Jun;213:63-75. 2016 Feb 12.

Reidel, G.F., Abbe G.R., Sanders J.G., (1995). Silver and copper accumulation in two estuarine bivalves, the eastern oyster (Crassostrea virginica) and the hooked mussel (Ischadiumrearrum). Estuaries, 18, 445-455.

Ridgeway J., Shimmield G., (2002). Estuaries as repositories of historical contamination and their impact on shelf seas. Estuarine, coastal and shelf science 55, 903–928.

ROM: Recommendations for Maritime Works, (2013). ROM 5.1-13: Quality of coastal waters in port areas, available: http://www.puertos.es/es-es/BibliotecaV2/ROM%205.1-05%20(EN).pdf

Rostmark S.C., Colombo M., Knutsson S., Öberg G., (2015). Removal and re-use of tar-contaminated sediment by freeze-dredging at a coking plant Luleå, Sweden. Water environ. res. 2016;88(9):847-851. Epub 2015 Jul 13.

Alfonso S., (2014). GNL Quintero and its commitment with the community: Shaping a new Quintero, available: http://conferences.iaia.org/2014/IAIA14-final-ppers/Salinas,%20Alfonso.%20%20GNL%20Quintero%20and%20its%20commitment%20with%20the%20community.pdf

Salomons W., Förstner U. (1984). Metals in the hydrocycle. Springer-Verlag, Berlin, 688pp.

Sankar, T.V., Zynudheen A.A., Anandan R., Viswanathan P.G., (2006). Distribution of organochloride pesticides and heavy metal residues in fish and shellfish from Calicut region, Kerala, India. Chemosphere, 65: 583-590.

Schiff K.C., (2000). Sediment chemistry on the mainland shelf of the Southern California Bight. Marine pollution bulletin, 40, 268-270.

Selvaraj K., Ram M.V., Szefer P., (2004). Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. Marine pollution bulletin 2004; 49:174–85.

SETAC: Society of environmental toxicology and Chemistry (2002). Workshop; use of sediment quality guidelines and related tools for the assessment of contaminated sediments, Edited by Wenning R.J., Christopher G. Ingersoll C., 2002.

Soto M., (2001). Biodisponibilidad de metales pesados (Cd, Cu y Pb) en sedimentos marinos superficiales procedentes de las principales zonas ostrícolas del estado de Sonora. Tesis, Escuela de ingeniería química. Universidad de Sonora.

Soto-Jiménez M.F., (2011). Transferencia de elementos traza en tramas tróficas acuáticas. Hidrobiológica 21: 239-248.

Shiomi K., (1994). Arsenic in marine organisms: chemical forms and toxicological aspects. In: Nriagu JO eds. Arsenic in the Environment, Part II: Human Health and Ecosystem Effect*s.* NewYork: Wiley J., Sons, Inc.: 261-282.

Spellman F.R., (2016). Contaminated sediments in freshwater systems, CRC Press, 16.10.2016.

Streit, B., (1998). Bioaccumulation of contaminants in fish. EXS. 1998;86:353-87. Review.

Stern B.R., (2010). Essentiality and toxicity in copper health risk assessment: overview, update and regulatory considerations. Toxicol. environ. health A. 2010;73(2):114–127.

SYKE Suomen ympäristökeskus (2016). Itämeren ympäristömyrkkyjen seuranta available (referred 20.12.2016): http://www.ymparisto.fi/fi-FI/Meri/Itameren_tilan_seuranta/Ymparistomyrkkyjen_seuranta

Tchounwou P.B., Ayensu W.K., Ninashvilli N., Sutton D., (2003). Environmental exposures to mercury and its toxicopathologic implications for public health. Environ Toxicol. 2003;18:149–175.

Terram Fundation (2014). Ministro Badenier: “El derrame del 24 de septiembre no va a quedar impune”. Quintero, Chile

Tornero V., Hanke G., (2016). Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas. Marine pollution bulletin 2016; 112:17-38.

Uluturhan E., Kucuksezgin F., (2007). Heavy metal contaminants in red pandora (Pagellus erythrinus) tissues from the Eastern Aegean Sea, Turkey. Water Res 41:1185-1192.

UNEP: United Nations Environment Program, (2013). Environmental risks and challenges of anthropogenic metals flows and cycles.

US EPA: United States Environmental Protection Agency, (1997). Ecological risk assessment guidance for superfund: process for designing and conducting ecological risk assessments, interim final. Environmental response team, Edison, NJ, EPA 540-R-97-006. Available: https://www.epa.gov/superfund/programs/risk/ecorisk/ecorisk.htm

US EPA: United States Environmental Protection Agency, (1998). EPA's contaminated sediment management strategy. 823/R98/001. Washington, D.C.

US EPA: United States Environmental Protection Agency (2004). "Contaminated sediment in water." Fact sheet. Available: http://www.epa.gov/waterscience/cs/aboutcs.

US EPA: United States Environmental Protection Agency, (2004b). National coastal condition report II, EPA-620/R-03/002. U.S. Environmental Protection Agency, Washington, DC. Available: http://www.epa.gov/owow/oceans/nccr/2005/downloads.html.

US EPA: United States Environmental Protection Agency, (2005). Contaminated sediment remediation quidance for hazardous waste sites. Available: https://semspub.epa.gov/work/HQ/174471.pdf

US EPA: United States Environmental Protection Agency, (2007). Aquatic life ambient freshwater quality criteria - copper. 2007 Revision. EPA-822-R-07-001 (CAS Registry no. 7440-50-8). Washington DC: US Environmental Protection Agency (EPA) and Office of Water.

Urrutia J.S., Avilés S., (2017). Environmental law and practice in Chile: overview. Available (referred 9/5/2017): https://uk.practicallaw.thomsonreuters.com/1-503-4725?transitionType=Default&contextData=(sc.Default)&firstPage=true&bhcp=1

Vallius H., Ryabchuk D., Kotilainen A., (2007). Distribution of heavy metals and arsenic in soft surface sediments of the coastal area off Kotka, northeastern Gulf of Finland, Baltic Sea. In: Vallius, H. (ed.) Holocene sedimentary environment and sediment geochemistry of the eastern Gulf of Finland, Baltic Sea. Geological Survey of Finland, Special Paper 45, 33–48.

Warmer H., Dokkum R., (2002). Water pollution control in the Netherlands, policy and practice 2001, March 2002 RIZA report 2002.009.

Wenning R.J., Batley G.E., Ingersoll C.G., Moore D.W., (2005). Use of sediment quality guidelines & related tools for the assessment of contaminated sediments (SQG). Summary booklet of a SETAC Pellston workshop.

WHO: World Health Organization, (1996). Switzerland: Geneva trace elements in human nutrition and health. Available: http://www.who.int/nutrition/publications/micronutrients/9241561734/en/

Wright D.A., Welbourn P., (2002). Environmental toxicology. Cambridge University Press, Cambridge, U.K.